

IN THE UNITED STATES DISTRICT COURT  
FOR THE DISTRICT OF DELAWARE

CIBA SPECIALTY CHEMICALS	)	
CORPORATION, a Delaware Corporation,	)	
	)	C.A. No.
Cross-Plaintiff	)	
	)	
	)	
v.	)	
	)	
	)	
3V, INC., a Delaware Corporation,	)	
	)	
Cross-Defendant	)	
	)	

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**CROSS-COMPLAINT**

**Jurisdiction and Venue**

1. This cross-suit arises under the patent laws of the United States, 35 United States Code, and seeks review to remedy a final decision dated July 27, 2006, of the Board of Patent Appeals and Interferences of the United States Patent and Trademark Office ("Board") in patent interference proceeding No. 105,262. This decision was partially adverse to cross-plaintiff CIBA Specialty Chemicals Corporation, holding that cross-plaintiff's claims 16-27 were not entitled to the benefit of priority based upon European priority application EP 95810042.2.

2. Review by this Court is specifically provided under 35 U.S.C. § 146 and 37 C.F.R. § 1.304. Jurisdiction of this action lies with this court under 28 U.S.C § 1331 and 28 U.S.C. § 1338(a).

3. This matter is timely brought in view of the decision of the Board entered on July 27, 2006 and the Complaint served by cross-defendant. No appeal has been taken to the United States Court of Appeals for the Federal Circuit. Venue is proper in this district pursuant to § 1391 (b) and (c).

### The Parties

4. Cross-Plaintiff CIBA Specialty Chemicals Corporation ("CIBA") is a corporation of the State of Delaware having a principal place of business located at 540 White Plains Road, Tarrytown, New York.

5. Upon information and belief, Defendant 3V, Inc. ("3V") is a Delaware corporation having a principal place of business at 899 Woodstock Street, Georgetown, South Carolina.

6. Upon information and belief 3V, is the assignee of all right, title and interest in U.S. Patent 5,658,973 (the '973 patent), involved in the aforesaid interference. The '973 Patent names Giuseppe Raspanti of Bergamo, Italy, as inventor.

7. CIBA is the assignee of all right, title and interest to the invention relating to a "Synergistic Stabilizer Mixture" which is disclosed and claimed in U.S. Patent Application Serial No. 10/081,291, filed February 22, 2002 (the '291 application), which was accorded benefit of U.S. Application Serial No. 09/275,859, filed March 24, 1999; U.S. Application Serial No. 08/858,191, filed April 21, 1997; U.S. Application Serial No. 08/588,164, filed January 18, 1996; and, European Application No. 95810042.2 filed January 23, 1995. The '291 application names Francois Gugumus as inventor.

8. On May 24, 2005, the Board originally declared Interference No. 105,262 between Giuseppe Raspanti the named inventor of the '973 Patent, involved in the interference and Francois Gugumus the named inventor of U.S. Patent Application Serial No. 10/081,291.

9. Upon information and belief 3V, has all right, title and interest in the '973 Patent, which issued on August 19, 1997; and, is a real party in interest in the interference as shown by

papers filed by counsel for 3V in the interference. A copy of the '973 Patent is attached hereto as Exhibit 1.

10. CIBA has all right, title and interest in the '291 application filed on February 22, 2002, and is a real party in interest. A copy of the '291 application is attached hereto as Exhibit 2.

11. Count I of the interference reads as follows:

Count I: A COMPOSITION according to claim 1 of Raspanti (5,658,973) comprising a compound a) and compound b) in a weight ratio of 1:1, wherein:

a) is a compound of formula (X) of claim 4 of Raspanti where:

r is 2 or 3,

R in formula (III) is hydrogen and

p is 2 to 20

and

b) is a compound of formula (V) of claim 4 of Raspanti where:

R is hydrogen or methyl,

n is 1 to 10 and

p is 2 to 50

or

a method for stabilizing synthetic polymers comprising the step of adding to a polyolefin in an effective stabilizing amount of the COMPOSITION,

or

a stabilized polymer comprising a polyolefin and the COMPOSITION.

12. On July 27, 2006, the Board entered a final decision. In its final decision, the Board, erroneously, and contrary to law, granted Raspanti's (3V's) Substantive Motion 4 (Paper No. 35) for judgment that Gugumus (CIBA) claims 16-27 are unpatentable under 35U.S.C.102(e) as anticipated by Raspanti's '973 patent. In its decision, the Board erroneously held that the Gugumus claims 16-27 were not entitled to the benefit of priority based upon European priority application EP 95810042.2 due to a lack of a written description in the European application of the full scope of the subject matter recited in the Gugumus claims. The Board erroneously failed to recognize that the disclosure of the European application, together with the knowledge of those skilled in the art at the time of the filing of the European application, were sufficient to constitute a sufficient enabling written description of the subject matter of the Gugumus claims pursuant to 35 U.S.C. § 112, first paragraph.

13. CIBA preserves all the issues raised in its motions in the U.S. Patent and Trademark Office as they relate to Count I.

## COUNTS

14. This is a Cross-Complaint action pursuant to 35 U.S.C. § 146 and C.F.R. 1.304 that CIBA is entitled to certain patent claims in its application 10/081,291 in interference.

15. CIBA repeats and realleges the allegations contained in paragraphs 1 through 14 of this Complaint as if fully set forth herein.

WHEREFORE, PLAINTIFF prays that the Court grant:

- A. Leave to introduce the record of Interference No. 105,262 before the Board and to take discovery and introduce additional evidence to supplement the record in this action;
- B. *De novo* consideration by this Court of the Interference record, if introduced, and the supplemental evidence, with respect to the issues of patentability and affirm CIBA's priority

as to Count I and other matters as referenced herein or which CIBA asserts are related to this matter.

C. Judgment awarding priority to Cross-Plaintiff CIBA with respect to Count I.

D. Judgment ordering that:

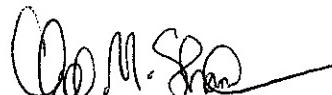
(i) claims 16-27 of the '291 application are patentable to CIBA (Gugumus);

and; that:

(ii) claims 16-27 are entitled to priority based upon the earlier European application EP 95810042.2.

E. That the Clerk of this Court shall issue a certified copy of this court's judgment for transmittal to the U.S. Patent and Trademark Office, and that the Director of the U.S. Patent and Trademark Office shall be authorized fully to implement this Court's order.

F. Judgment ordering any further relief as may be equitable and/or appropriate in order to preserve the rights of CIBA in any further proceedings on remand before the U.S. Patent and Trademark Office.



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Dated: October 10, 2006



**United States Patent [19]**

Raspanti

[11] Patent Number: 5,658,973

[45] Date of Patent: Aug. 19, 1997

## [54] COMPOSITIONS FOR THE STABILIZATION OF SYNTHETIC POLYMERS

[75] Inventor: Giuseppe Raspanti, Bergamo, Italy

[73] Assignee: 3V Inc., Weehawken, N.J.

[21] Appl. No.: 507,197

[22] Filed: Jul. 26, 1995

[51] Int. Cl.<sup>6</sup> C08K 5/54; C08K 5/3492; C08K 5/3435

[52] U.S. Cl. 524/99; 252/405; 524/100; 524/102; 524/103

[58] Field of Search 524/100, 99, 102, 524/103; 252/405

## [56] References Cited

## U.S. PATENT DOCUMENTS

4,086,204	4/1978	Cassandrini et al.	544/198
4,108,829	8/1978	Cassandrini et al.	544/198
4,233,412	11/1980	Rody et al.	525/167
4,331,586	5/1982	Hardy	524/97
4,477,615	10/1984	Raspanti et al.	524/100
4,692,486	9/1987	Gugumus	524/100
4,863,981	9/1989	Gugumus	524/100
4,927,930	5/1990	Cantatore et al.	544/198
4,933,451	6/1990	Cantatore et al.	524/100
5,021,485	6/1991	Gugumus	524/100

## FOREIGN PATENT DOCUMENTS

343717	11/1989	European Pat. Off.	.
57-38589	8/1982	Japan .	

## OTHER PUBLICATIONS

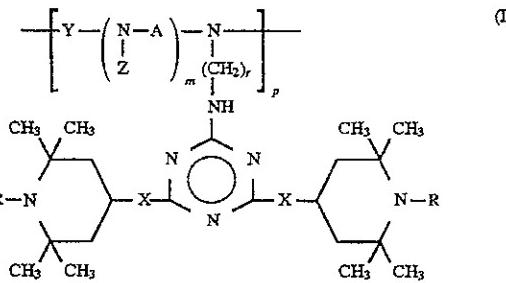
Tomoyuki Kurumada, et al., "Synergism of Hindered Amine Light Stabilizers and UV-Absorbers", Polymer Degradation and Stability 19 (1987) 263-272.

Primary Examiner—Veronica P. Hoke  
Attorney, Agent, or Firm—Griffin, Butler, Whisenhunt & Kurtossy

## [57] ABSTRACT

A composition for stabilizing synthetic polymers consisting of a blend of

a) at least a derivative of a high molecular weight polymethylpiperidine of formula (I)



wherein the groups are as defined hereinafter, and  
b) at least one other HALS stabilizer wherein the groups are as defined hereinafter is disclosed. These compositions show photostabilizing and antioxidant properties.

15 Claims, No Drawings

5,658,973

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**COMPOSITIONS FOR THE STABILIZATION  
OF SYNTHETIC POLYMERS**

The present invention relates to compositions consisting of mixtures of two or more different derivatives of high molecular weight polymethylpiperidine and to their use as stabilizing agents for synthetic polymers.

**BACKGROUND OF THE INVENTION**

The use of compounds containing the polymethylpiperidine group, and mainly 2,2,6,6-tetramethyl-*o*-1,2,2,6,6-pentamethylpiperidine, for the photostabilization of polymers is well known and to this end a wide literature exists.

Generally this class of stabilizing agents is divided into two groups, namely those having low molecular weight (about 700) and those with high molecular weight (higher than 700).

A detailed disclosure of some stabilizing agents of this class, the so called hindered amines, of their different kinds and of their applicative characteristics is found in Gaechter-Mueller/Taschenbuch der Kunststoff-Additive, 2 Ausgabe 1983 pagg. 144-198.

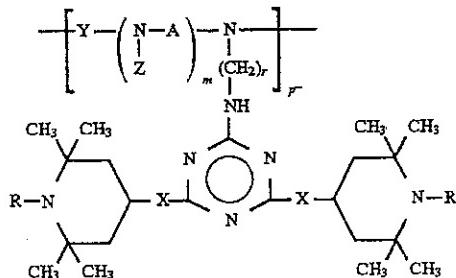
U.S. Pat. Nos. 4,692,486, 5,021,485 and EP 0080431 disclose some synergistic mixtures of derivatives of low and high molecular weight polyalkylpiperidines as photostabilizing agents for polymers. U.S. Pat. No. 4,863,981 discloses also mixtures containing two different derivatives of polymethylpiperidine, both of them having high molecular weight, as photostabilizing agents for polymers.

It has surprisingly been found that new particular combinations of compounds, all of them having high molecular weight, containing polymethylpiperidine groups, in addition to synergistic properties as photostabilizing agents, also show synergistic activity in the long term heat stabilization of synthetic polymers. As used herein, the wording "long term heat stabilization" is intended to mean that the polymer is stabilized against the degradation which occurs during the time of use of the polymer itself. As far as it is known to the applicant, said synergistic activity in the long term heat stabilization was not disclosed nor suggested in the prior art.

**DISCLOSURE OF THE INVENTION**

An object of the present invention is a composition for the stabilization of synthetic polymers consisting of a mixture of:

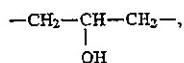
a) at least a compound of formula (I)



wherein R is hydrogen or methyl, X is oxygen or the N-R<sub>1</sub> group, in which R<sub>1</sub> is hydrogen or a C<sub>1</sub>-C<sub>12</sub> straight or branched alkyl, r is a number ranging from 2 to 8, included;

A is -(CH<sub>2</sub>)<sub>n</sub>-, in which n can be a number from 2 to 8, the group

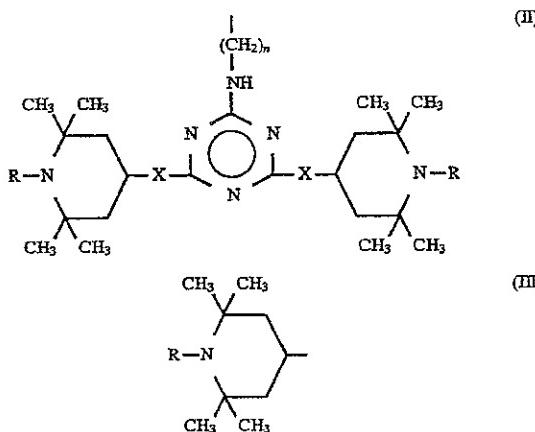
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or the group



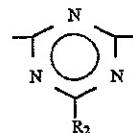
Z is hydrogen, C<sub>1</sub>-C<sub>18</sub> alkyl, the group of formula (II) or the piperidine of formula (III):



wherein R, X and n have the above defined meaning;

m is zero or 1;

Y, when m is zero, has the same meaning of A, when m is 1 can have the same meaning of A or is one of the following groups



-CO-R<sub>3</sub>-CO; -CO-NH-R<sub>4</sub>-NH-CO- in which R<sub>2</sub> is an optionally substituted aryl residue, having from 6 to 14 carbon atoms or the



group in which R<sub>5</sub> and R<sub>6</sub> can be the same or different and are hydrogen, a C<sub>1</sub>-C<sub>18</sub> straight or branched alkyl group, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 7 to 12 carbon atoms; the piperidine group of formula (III) or, together the nitrogen atom which they are linked to, can form a heterocyclic ring having from 5 to 7 members, optionally containing also oxygen as heteroatom;

R<sub>3</sub> is phenylene or -(CH<sub>2</sub>)<sub>n</sub>-;

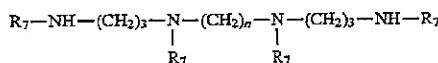
R<sub>4</sub> is tolylene, xylylene or -(CH<sub>2</sub>)<sub>n</sub>-, in which n has the above defined meaning;

p can vary from 2 to 100; the terminal groups can be Cl or H; and

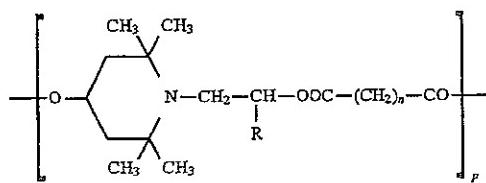
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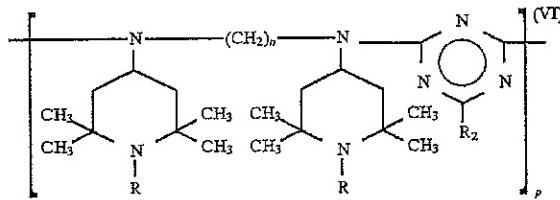
b) at least a compound of formula (IV), (V); (VI) or (VII)



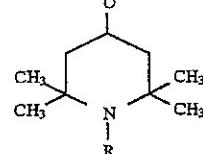
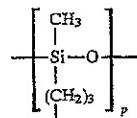
(IV)



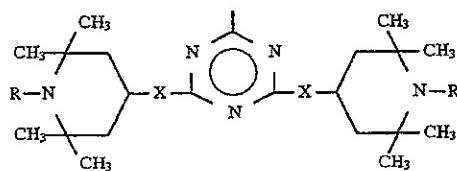
(V)



(VI)



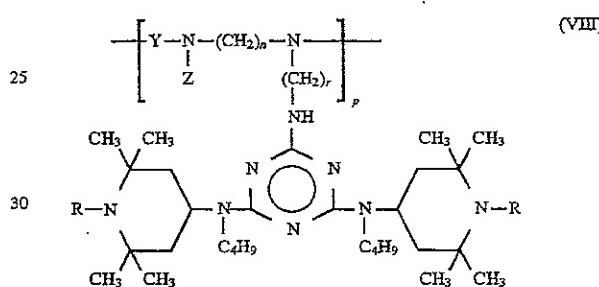
(VII)

wherein  $\text{R}_7$  is a group of formula

wherein X and R are as above defined;

R,  $\text{R}_2$ , n and p have the above meaning, the terminal groups  
can be hydrogen for compounds (V), chlorine or hydro-  
gen for compounds (VI) and methyl for compounds (VII).Examples of  $\text{C}_1-\text{C}_{18}$  straight or branched alkyl group are  
methyl, ethyl, n-propyl, isopropyl, n-butyl, tert-butyl,  
pentyl, neo-pentyl, hexyl, heptyl, decyl, dodecyl, hexadecyl,  
octadecyl.Examples of optionally substituted aryl group having  
from 6 to 14 carbon atoms are phenyl, toluyl, o-, m-, p-xylyl.

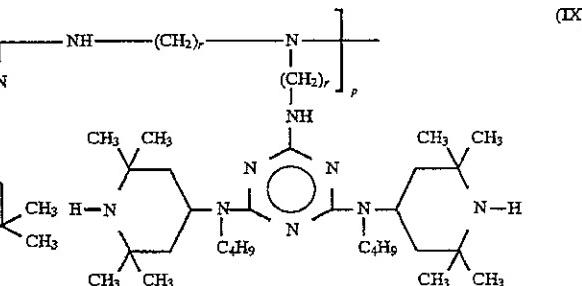
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Examples of cycloalkyl group having from 5 to 12 carbon  
atoms are cyclopentyl, cyclohexyl, cyclododecyl.Examples of aralkyl group having from 7 to 12 carbon  
atoms are benzyl, 4-tert-butylbenzyl.Examples of heterocyclic group having from 5 to 7  
members are: pyrrolidine, piperidine, hexamethyleneimine,  
morpholine.The compounds of formula (I), (IV), (V), (VI) and (VII)  
are known; their methods of preparation as well as their uses  
as stabilizing agents are described in patents U.S. Pat. Nos.  
4,477,615, 4,233,412, 4,108,829, 4,086,204, 4,331,586, EP  
0255181.However, the stabilizing compositions according to the  
present invention show a photoprotective activity higher  
than the single components of formula (I) or (IV-VII).In a first preferred embodiment of the present invention,  
the component a) is represented by the compound of formula  
(VIII)

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wherein Z, Y, R, n and p have the above defined meaning;  
r is 2 or 3.In a second preferred embodiment of the present  
invention, the component a) is represented by the compound  
of formula (IX)

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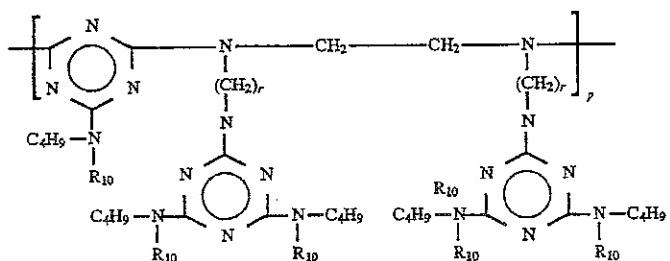
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wherein r and p are as above defined.

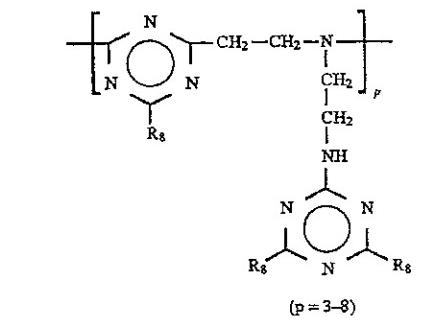
In a third preferred embodiment of the present invention, the component a) is represented by the compound of formula (X)



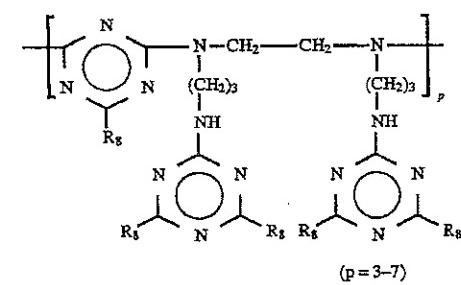
(X)

wherein r and p are as above defined, R<sub>10</sub> is a group of formula (III).

Examples of compounds of formula I are:

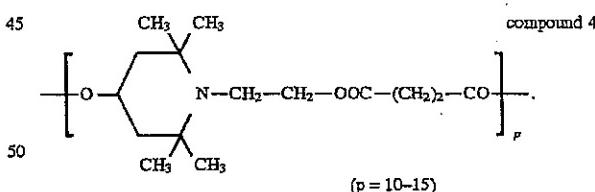
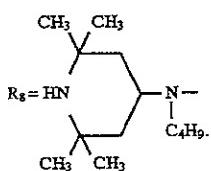


compound 1  
20  
25

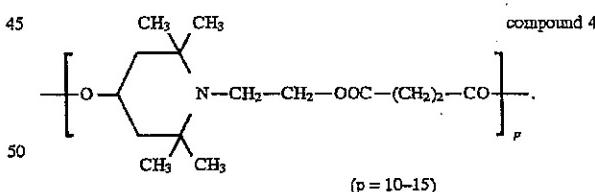


compound 2  
30  
35

wherein



An example of compound of formula V is:



Examples of compounds of formula VI are:

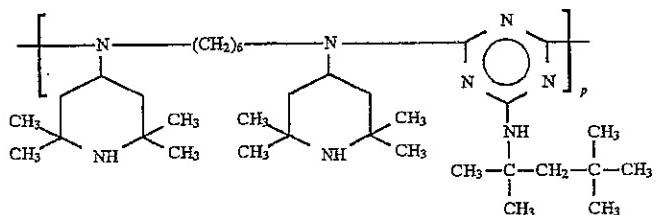
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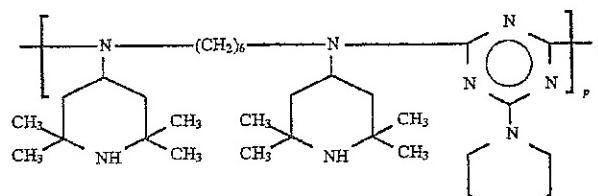
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(p = 8-14)

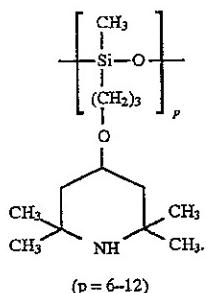
compound 5



(p = 8-15)

compound 6

An example of compound of formula VII is:



(p = 6-12)

compound 7 25

metal deactivators, for example oxalic acid amides, plasticizers, antistatic agents, pigments, optical bleaching agents, flame retarders.

The following examples further disclose the present invention.

#### EXAMPLE 1

30 1.000 g of low density polyethylene (Riblene EF 2100 V-Enichem®), 2 g of n-octadecyl-3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate, 1 g of calcium stearate and 1 g of a stabilizing agent, according to the present invention, or of a mixture thereof in 50:50 w/w ratio, were mixed homogeneously. The mixtures were extruded at 190° C. and transformed into pellets. From these pellets, by means of pressure forming at 200° C., films of 0.2 mm thickness were obtained.

40 Samples of these films were subjected to UV radiation in a Weatherometer WOM Ci-65® at a black panel temperature of 63° C. In the irradiated samples the increase of the carbonyl band at 5.85 nm in the infrared was measured and the T-0.1, i.e. the time necessary to give an increase of 0.1 of the carbonyl band, was determined. The results are reported in the following Table 1.

TABLE 1

Stabilizing agent	T 0.1 (hours)
Without stabilizing agent	300
Compound 1	2100
Compound 2	2000
Compound 3	1950
Compound 4	1750
Compound 5	2100
Compound 7	1650
Compounds 1 + 3	2750
Compounds 1 + 4	2850
Compounds 1 + 5	2650
Compounds 2 + 5	2800
Compounds 1 + 7	2600
Compounds 4 + 5 (according to US 4 863 981)	2800

#### EXAMPLE 2

65 Homogeneous mixtures, consisting of 1,000 g of polypropylene, (Moplen FLF 20-Himont®), 1 g of 1,3,5-tris-(3,5-di-tert-butyl-4-hydroxybenzyl)isocyanurate, 0.5 g

The concentration of the stabilizing compositions according to the present invention in the polymers can generally vary from 0.01 to 5% and preferably from 0.05 to 2% with respect to the weight of the polymer. Nevertheless, the stabilizing mixture can be added to the polymers also in very high amounts, for example 5-25% by weight, for the preparation of masterbatches.

The incorporation can be carried out according to various methods, for example by dry mixing the polymer with the stabilizing mixture or said mixture can be added to a suspension of the polymer to be stabilized in a suitable solvent and subsequently evaporating off the solvent.

Subsequently the polymers containing the stabilizing mixture are extruded or treated according to methods usually known in the art.

According to the present invention the compositions of compounds of formula (I) and respectively of formula (IV)-(VII) are used for the stabilization of synthetic polymers, particularly of polyolefins such as for example 55 low and high density polyethylene, polypropylene, polymethylpentene, polyisoprene, polystyrene, polymethylstyrene and copolymers thereof and/or with other vinyl monomers as for example acrylonitrile, vinyl acetate, acryl esters.

The stabilizing compositions according to the present invention can be used also together with other additives commonly used in the technology of the synthetic polymers, such as for example: antioxidants, for example those belonging to the classes of phenols, thioethers, phosphites and phosphonites; UV-absorber, for example oxanilydes, benzotriazole and benzophenone derivatives; nickel complexes;

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of calcium stearate and 2 g of a stabilizing agent or of a 50:50 mixture thereof were prepared. The mixtures were extruded at 250° C. and granulated. From these, by means of pressure forming at 260° C., 1 mm thickness-test pieces were obtained.

The so obtained test pieces were subjected to atmospheric oxygen action by heating at 130° C. in a forced air circulation oven.

The degradation was evaluated by determining the time necessary for the "chalky" appearance on test pieces.

The results are reported in the following Table 2.

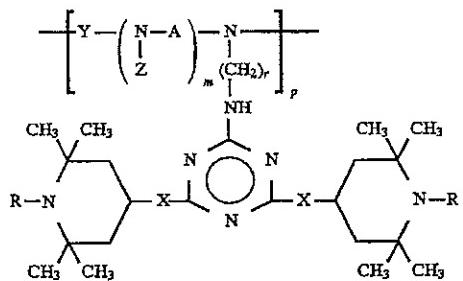
TABLE 2

Stabilizing agent	T (days)
Without stabilizing agent	34
Compound 1	55
Compound 2	57
Compound 3	49
Compound 4	54
Compound 5	57
Compound 7	41
Compounds 1 + 3	85
Compounds 2 + 4	81
Compounds 1 + 5	80
Compounds 2 + 5	78
Compounds 1 + 7	76
Compounds 4 + 5 (according to US 4 863 981)	58

I claim:

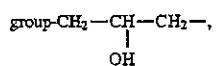
1. A composition for the stabilization of synthetic polymers comprising an about 1:1 ratio of the following components a) and b) wherein:

a) is at least one compound of formula (I)



wherein R is hydrogen or methyl, X is oxygen or the group N—R<sub>1</sub>, in which R<sub>1</sub> is hydrogen or C<sub>1</sub>—C<sub>12</sub> straight or branched alkyl group, r is a number ranging from 2 to 8, included;

A is —(CH<sub>2</sub>)<sub>n</sub>—, in which n can be a number from 2 to 8, the



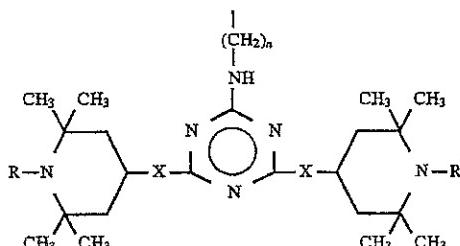
or the group



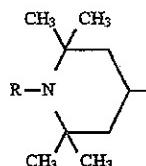
Z is hydrogen, C<sub>1</sub>—C<sub>18</sub> alkyl, the group of formula (II) or the piperidine of formula (III)

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(II)

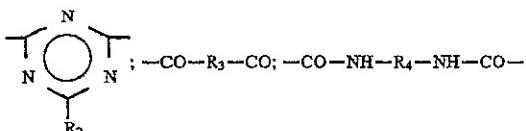


(III)

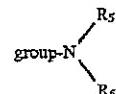


wherein R, X and n have the meaning above defined; m is zero or 1;

Y, when m is zero, has the same meaning of A, when m is 1 can have the same meaning of A or is one of the following groups



in which R<sub>2</sub> is an optionally substituted aryl residue, having from 6 to 14 carbon atoms or the



in which R<sub>5</sub> and R<sub>6</sub> can be the same or different and are hydrogen, a C<sub>1</sub>—C<sub>18</sub> straight or branched alkyl group, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 7 to 12 carbon atoms; the piperidine group of formula (III) or, together the nitrogen atom, can form a 5 to 7 member heterocyclic ring, optionally containing oxygen as heteroatom;

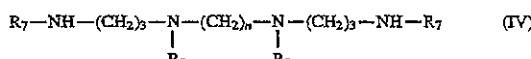
R<sub>3</sub> is phenylene or —(CH<sub>2</sub>)<sub>n</sub>—;

R<sub>4</sub> is tolylene, xylylene or —(CH<sub>2</sub>)<sub>n</sub>—, in which n has the above defined meaning,

p can range from 2 to 100;

the terminal groups can be Cl or H; and

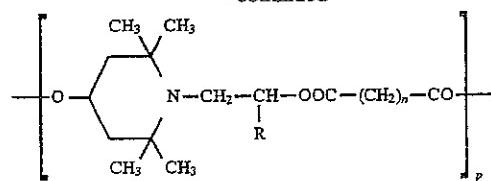
b) is at least one compound of formula (IV), (V), (VI) or (VII)



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**11**

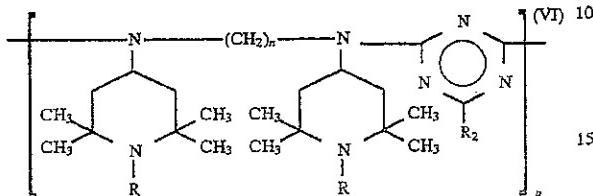
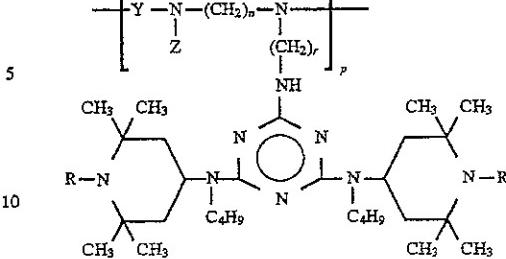
-continued



(V)

**12**

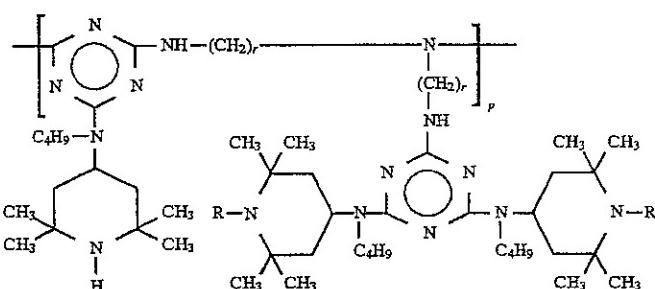
(VIII)



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wherein Z, Y, R, n and p are as above defined, r is 2 or 3.

3. A composition according to claim 1, wherein said compound a) is a compound of formula (IX), and said compound b) is a compound of formula (IV)-(VII)

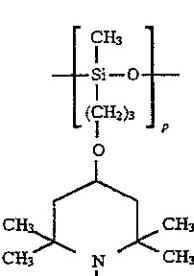


(IX)

wherein r and p are as above defined.

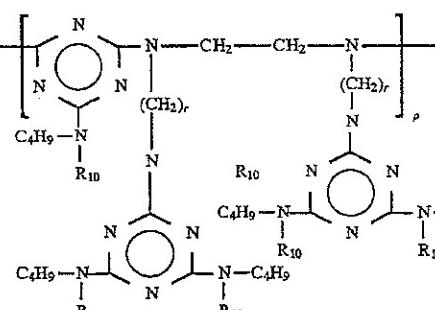
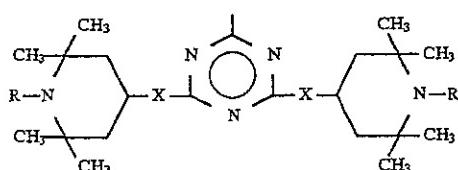
4. A composition according to claim 1, wherein a) is a compound of formula (X) and b) is a compound of formula (IV)-(VII)

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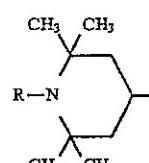
(VII)

(X)

wherein R<sub>7</sub> is a group of formula

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(III)



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wherein R is as above defined.

5. Masterbatch for the stabilization of synthetic polymers containing from 5 to 25% by weight of composition of claim 1.

6. A composition according to claim 1, consisting of a) and b).

7. A method for stabilizing synthetic polymers, comprising the step of adding to a polyolefin an effective stabilizing

wherein R, X, n and p are as above identified.

2. A composition according to claim 1, wherein said compound a) is a compound of formula (VIII), and said compound b) is a compound of formula (IV)-(VII)

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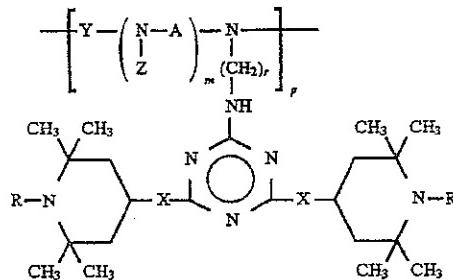
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amount of a composition comprising an about 1:1 ratio of the following components a) and b) wherein:

a) is at least one compound of formula (I)

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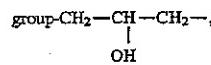
(I)

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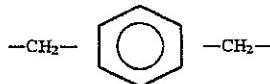
wherein R is hydrogen or methyl, X is oxygen or the group N—R<sub>1</sub>, in which R<sub>1</sub> is hydrogen or C<sub>1</sub>—C<sub>12</sub> straight or branched alkyl group, n is a number ranging from 2 to 8, included;

A is —(CH<sub>2</sub>)<sub>n</sub>—, in which n can be a number from 2 to 8, the

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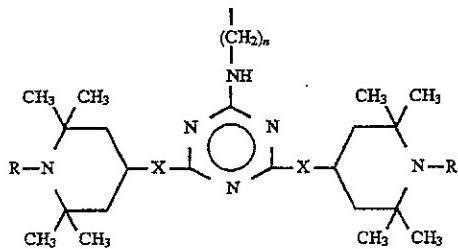
or the group



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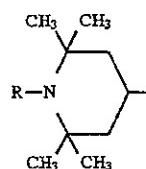
Z is hydrogen, C<sub>1</sub>—C<sub>18</sub> alkyl, the group of formula (II) or the piperidine of formula (III)

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(II)

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(III)

45

wherein R, X and n have the meaning above defined; m is zero or 1;

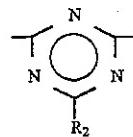
Y, when m is zero, has the same meaning of A, when m is 1 can have the same meaning of A or is one of the following groups

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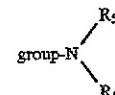
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—CO—R<sub>3</sub>—CO; —CO—NH—R<sub>4</sub>—NH—CO— in which R<sub>2</sub> is an optionally substituted aryl residue, having from 6 to 14 carbon atoms or the



in which R<sub>5</sub> and R<sub>6</sub> can be the same or different and are hydrogen, a C<sub>1</sub>—C<sub>18</sub> straight or branched alkyl group, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 7 to 12 carbon atoms; the piperidine group of formula (III) or, together the nitrogen atom, can form a 5 to 7 member heterocyclic ring, optionally containing oxygen as heteroatom;

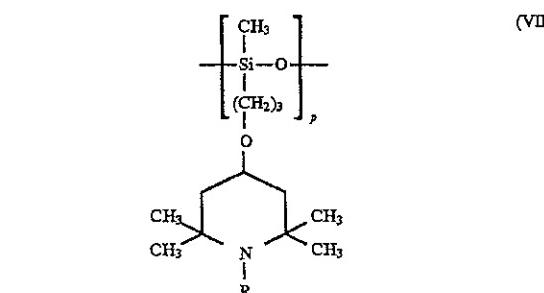
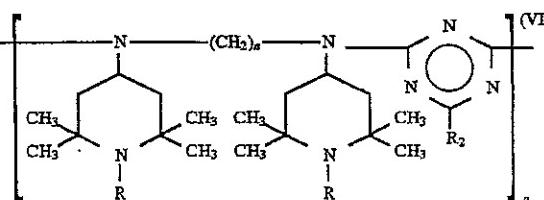
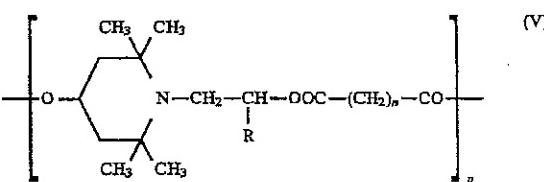
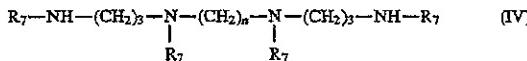
R<sub>3</sub> is phenylene or —(CH<sub>2</sub>)<sub>n</sub>—;

R<sub>4</sub> is toluylene, xylylene or —(CH<sub>2</sub>)<sub>n</sub>—, in which n has the above defined meaning,

p can range from 2 to 100;

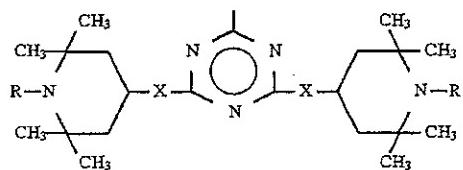
the terminal groups can be Cl or H; and

b) at least one compound of formula (IV), (V); (VI) or (VII)



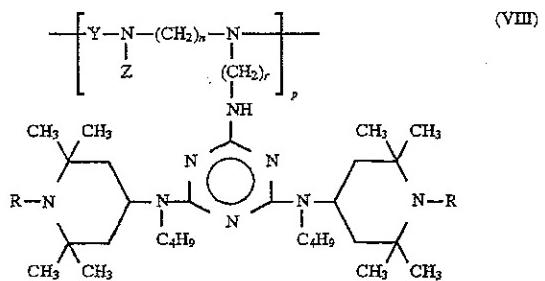
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wherein R<sub>7</sub> is a group of formula

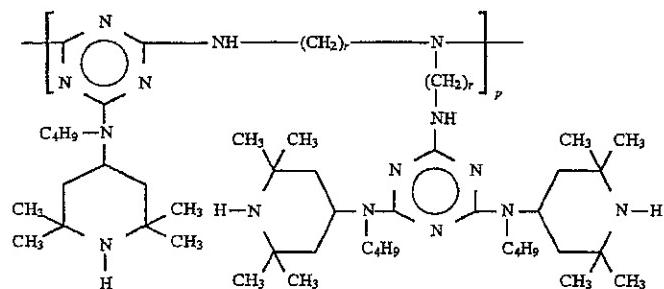
wherein R, X, n and p are as above identified.

8. A method for stabilizing synthetic polymers, according to claim 7, wherein said compound a) is a compound of formula (VIII),



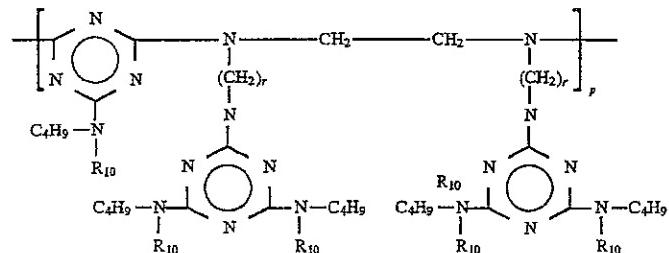
wherein X, Y, R, n and p are as above defined, r is 2 or 3.

9. A method according to claim 7, wherein said compound a) is a compound of formula (IX), and said compound b) is a compound of formula (IV)-(VII)

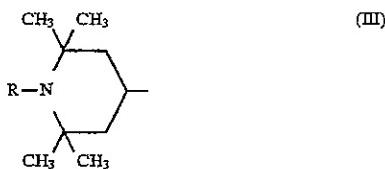


wherein r and p are as above defined.

10. A method according to claim 7, wherein a) is a compound of formula (X) and b) a compound of formula (IV)-(VII)

wherein r and p are as above defined and R<sub>10</sub> is a group of formula (III)

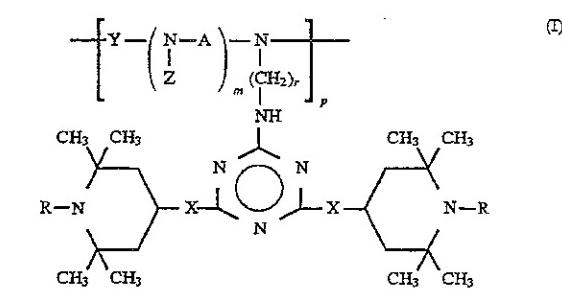
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wherein R is as above defined.

10 11. A stabilized polymer comprising a polyolefin and a composition for the stabilization of synthetic polymers comprising an about 1:1 ratio of the following components a) and b) wherein:

a) is at least one compound of formula (I)



wherein R is hydrogen or methyl, X is oxygen or the group N-R<sub>1</sub>, in which R<sub>1</sub> is hydrogen or C<sub>1</sub>-C<sub>12</sub> straight or branched alkyl group, r is a number ranging from 2 to 8, included;

(IX)

45 A is -(CH<sub>2</sub>)<sub>n</sub>-, in which n can be a number from 2 to 8, the

(X)

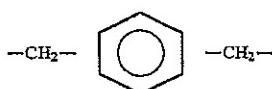
group-CH<sub>2</sub>-CH(OH)-CH<sub>2</sub>-,

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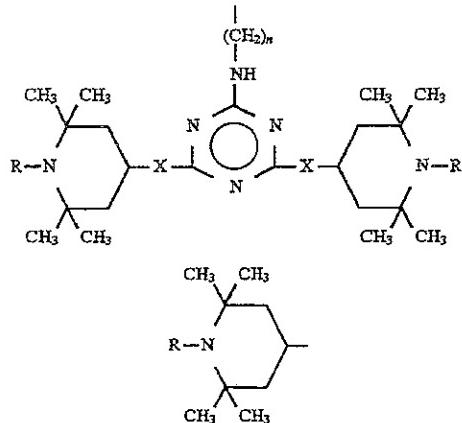
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or the group

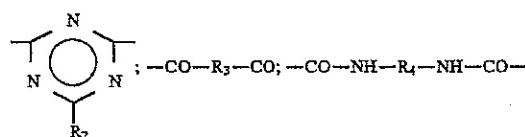


Z is hydrogen, C<sub>1</sub>-C<sub>18</sub> alkyl, the group of formula (II) or the piperidine of formula (III)

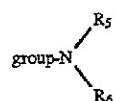


wherein R, X and n have the meaning above defined; m is zero or 1;

Y, when m is zero, has the same meaning of A, when m is 1 can have the same meaning of A or is one of the following groups



in which R<sub>2</sub> is an optionally substituted aryl residue, having from 6 to 14 carbon atoms or the



in which R<sub>5</sub> and R<sub>6</sub> can be the same or different and are hydrogen, a C<sub>1</sub>-C<sub>18</sub> straight or branched alkyl group, a cycloalkyl group having from 5 to 12 carbon atoms, an aryl group having from 6 to 12 carbon atoms, an aralkyl group having from 7 to 12 carbon atoms; the piperidine group of formula (III) or, together the nitrogen atom, can form a 5 to 7 member heterocyclic ring, optionally containing oxygen as heteroatom;

R<sub>3</sub> is phenylene or -(CH<sub>2</sub>)<sub>n</sub>;

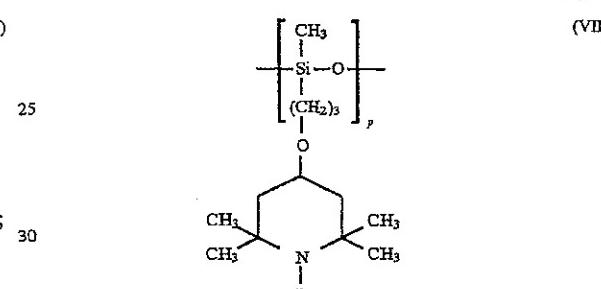
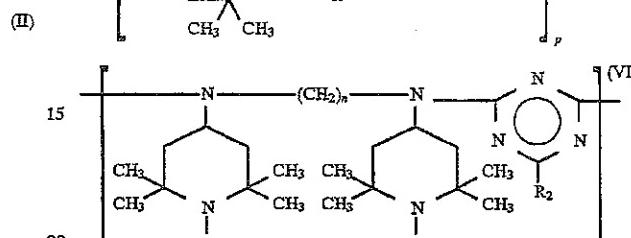
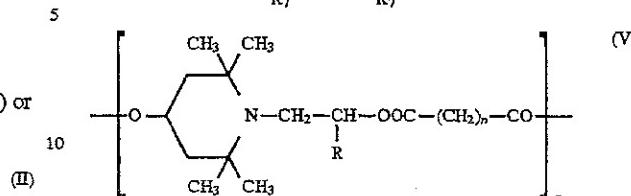
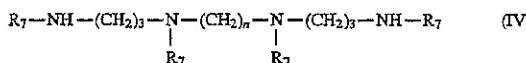
R<sub>4</sub> is tolylene, xylylene or -(CH<sub>2</sub>)<sub>n</sub>, in which n has the above defined meaning,

p can range from 2 to 100;

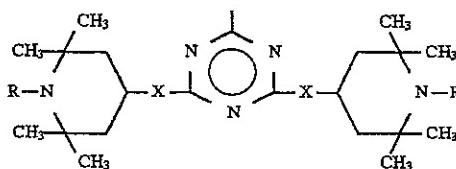
the terminal groups can be Cl or H; and

18

b) at least a compound of formula (IV), (V); (VI) or (VII)

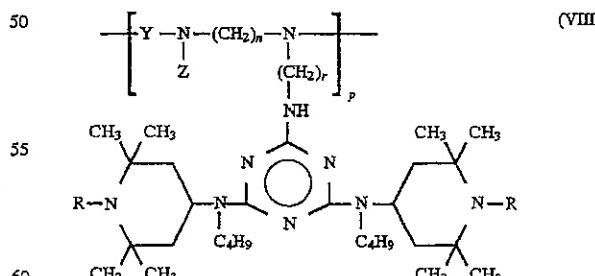


wherein R<sub>7</sub> is a group of formula



wherein R, X, n and p are as above identified.

12. A stabilized polymer according to claim 11 wherein said compound a) is a compound of formula (VIII), and said compound b) is a compound of formula (IV)-(VII)

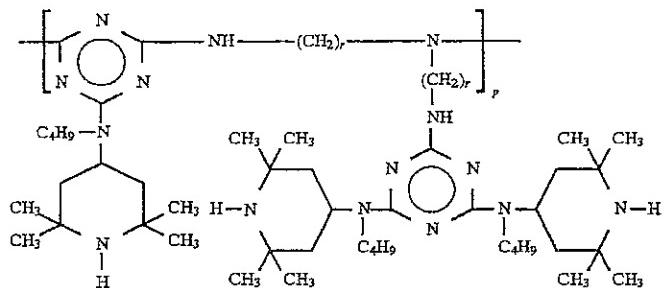


wherein Z, Y, R, n and p are as above defined, r is 2 or 3.

13. A stabilized polymer according to claim 11 wherein said compound a) is a compound of formula (IX), and said compound b) is a compound of formula (IV)-(VII)

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(IX)

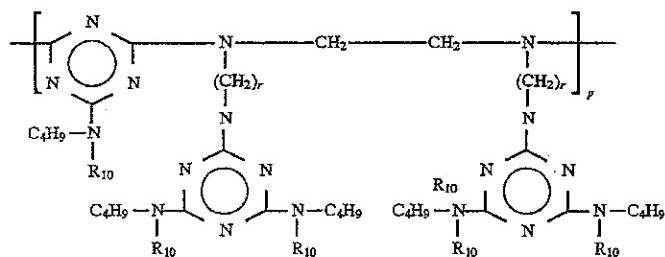
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wherein r and p are as above defined.

14. A stabilized polymer according to claim 11 wherein a) is a compound of formula (X) and b) is a compound of formula (IV)-(VII)

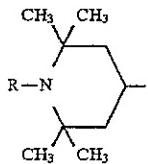
15 wherein R is as above defined.

15. A stabilized polymer according to claim 11 wherein said composition is present in an amount from 0.01 to 5% w-w.



(X)

wherein r and p are as above defined and R<sub>10</sub> is a group of formula (III)



(III) 35

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Exhibit 2

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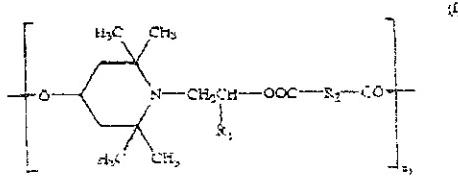
(19) United States

(12) Patent Application Publication (10) Pub. No.: US 2002/0120042 A1  
(43) Pub. Date: Aug. 29, 2002

## (54) SYNERGISTIC STABILIZER MIXTURE

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 CORPORATION  
 PATENT DEPARTMENT  
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 TARRYTOWN, NY 10591-9005 (US)



in which R<sub>1</sub> is hydrogen or methyl, R<sub>2</sub> is a direct bond or C<sub>1</sub>-C<sub>10</sub>alkylene, and n<sub>1</sub> is a number from 2 to 50, component b) is at least one compound of the formulae IIa and IIb

(21) Appl. No. 10/081,291

(22) Filed Feb. 22, 2002

## Related U.S. Application Data

(60) Continuation of application No. 09/275,859, filed on Mar. 24, 1999, now Pat. No. 6,380,286, which is a division of application No. 08/588,191, filed on Apr. 21, 1997, now Pat. No. 6,015,849, which is a continuation of application No. 08/588,164, filed on Jan. 18, 1996, now abandoned.

## (30) Foreign Application Priority Data

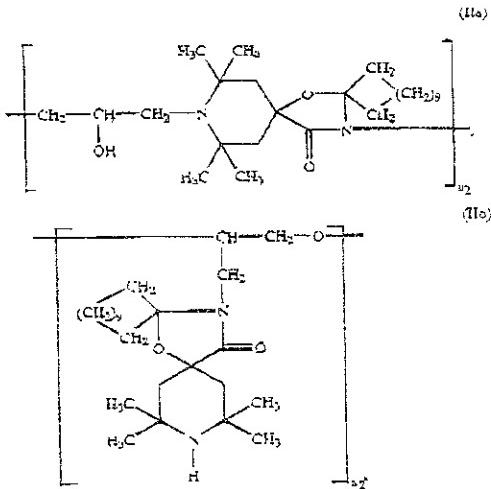
Jan. 23, 1995 (EP) 95810042.2

## Publication Classification

(51) Int. Cl.<sup>7</sup> C08K 5/34  
 (52) U.S. Cl. 524/102

## (57) ABSTRACT

A synergistic stabilizer mixture comprising a component a) and, for example, a component b), where component a) is at least one compound of the formula I



in which n<sub>2</sub> and n<sub>2\*</sub> are a number from 2 to 50.

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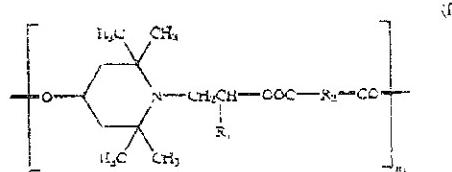
Aug. 29, 2002

## SYNERGISTIC STABILIZER MIXTURE

[0001] The present invention relates to a stabilizer system comprising two specific high-molecular-weight polyalkylpiperidine derivatives, to the use of this stabilizer system for stabilizing organic materials, and to the organic material protected against thermal, oxidative or light-induced degradation by means of the stabilizer system mentioned. U.S. Pat. No. 692,480, U.S. Pat. No. 4,863,981, U.S. Pat. No. 4,957,953, WO-A-92/12 281, EP-A-449 685, EP-A-632 092, GH-A-2 27 499 and Research Disclosure 34549 (January 1993) describe stabilizer mixtures comprising two polyalkylpiperidine derivatives.

[0002] The present invention relates to a stabilizer mixture comprising a component a) and a component b), c), d) or e), where

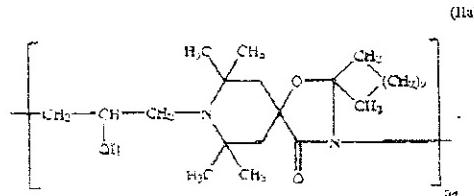
[0003] component a) is at least one compound of the formula I



[0004] in which R<sub>1</sub> is hydrogen or methyl,

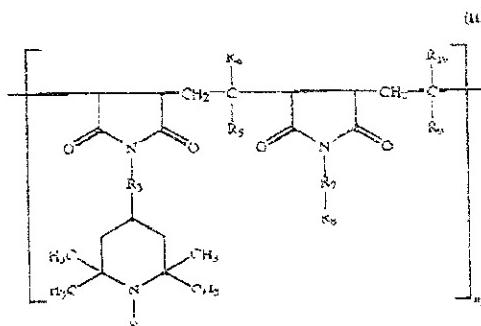
[0005] R<sub>2</sub> is a direct bond or C<sub>1</sub>-C<sub>6</sub>alkylene and n<sub>1</sub> is a number from 2 to 50,

[0006] component b) is at least one compound of the formulas IIa and IIb

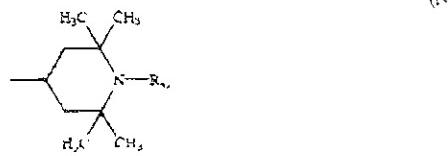


[0007] in which n<sub>2</sub> and n<sub>3</sub> are a number from 2 to 50;

[0008] component c) is at least one compound of the formula III



[0009] in which R<sub>5</sub> and R<sub>6</sub>, independently of one another, are a direct bond or an -N(X<sub>1</sub>)<sub>m</sub>-CO-X<sub>2</sub>-CO-N(X<sub>3</sub>)- group, where X<sub>1</sub> and X<sub>3</sub>, independently of one another, are hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>6</sub>-C<sub>12</sub>cycloalkyl, phenyl, C<sub>6</sub>-C<sub>12</sub>phenylalkyl or a group of the formula IV



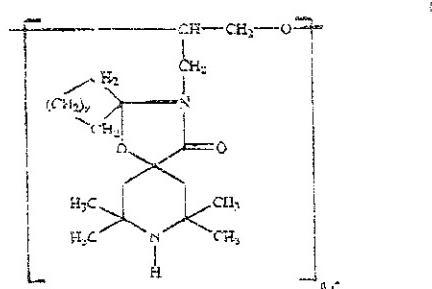
[0010] and X<sub>2</sub> is a direct bond or C<sub>1</sub>-C<sub>6</sub>alkylene, R<sub>7</sub> is hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, O, -CH<sub>2</sub>CN, C<sub>2</sub>-C<sub>6</sub>alkenyl, C<sub>6</sub>-C<sub>12</sub>phenylalkyl, C<sub>6</sub>-C<sub>12</sub>phenylalkyl which is substituted by C<sub>1</sub>-C<sub>6</sub>alkyl on the phenyl radical, or C<sub>1</sub>-C<sub>6</sub>acyl,

[0011] R<sub>8</sub>, R<sub>9</sub>, R<sub>10</sub> and R<sub>11</sub>, independently of one another, are hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>6</sub>-C<sub>12</sub>cycloalkyl or phenyl,

[0012] R<sub>8</sub> is hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>6</sub>-C<sub>12</sub>cycloalkyl, C<sub>6</sub>-C<sub>12</sub>phenylalkyl, phenyl or a group of the formula IV, and

[0013] n<sub>3</sub> is a number from 1 to 50,

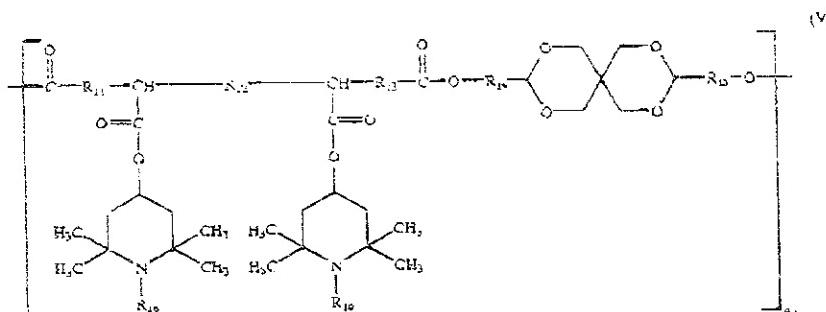
[0014] component d) is at least one compound of the formula V



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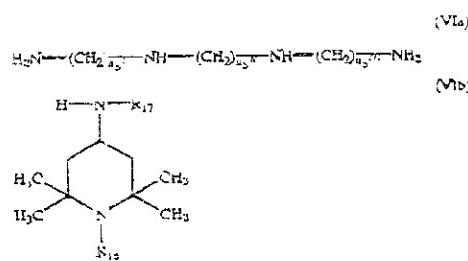
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[0015] in which  $R_{11}$ ,  $R_{12}$ ,  $R_{13}$  and  $R_{14}$ , independently of one another, are a direct bond or  $C_1-C_{10}$ alkylene,  $R_{10}$  is as defined for  $R_4$ , and  $n_1$  is a number from 1 to 50, and

[0016] component c) is a product obtainable by reacting a product obtained by reacting a polyamine of the formula VIa with cyanogen chloride, with a compound of the formula VIb



[0017] in which  $n_1$ ,  $n_2$  and  $n_3$ , independently of one another, are a number from 2 to 12,  $R_{17}$  is hydrogen,  $C_1-C_{12}$ alkyl,  $C_5-C_{12}$ cycloalkyl, phenyl or  $C_7-C_8$ phenylalkyl, and  $R_{18}$  is as defined for  $R_4$ .

[0018]  $n_1$ ,  $n_2$  and  $n_3$  are preferably from 2 to 4,  $R_{17}$  is  $C_1-C_4$ alkyl, and  $R_{18}$  is preferably hydrogen.

[0019] Examples of  $C_1-C_{10}$ alkylene are diethylene, ethylene, propylene, trimethylene, tetramethylene, pentamethylene, 2,2-dimethyltrimethylene, hexamethylene, trimethylhexamethylene, octamethylene and decamethylene.  $R_2$  is preferably ethylene,  $R_{12}$  and  $R_{13}$  are preferably methylene,  $R_3$  is preferably 2,2-dimethylethylene, and  $R_{15}$  is preferably 1,1-dimethylethylene.

[0020] Examples of alkyl having up to 30 carbon atoms are methyl, ethyl, propyl, isopropyl, n-butyl, sec-butyl, isobutyl, tert-butyl, 2-ethylbutyl, 2-pentyl, 2-pentenyl, 1-methylpentyl, 1,3-dimethylbutyl, n-hexyl, 1-methylhexyl, n-heptyl, isooctyl, 1,1,3,3-tetramethylbutyl, 1-methylheptyl, 3-methylheptyl, n-octyl, 2-ethylhexyl, 1,1,3-trimethylhexyl, 1,1,3,3-tetra-methylpentyl, nonyl, decyl, undecyl,

1-methylnonadecyl, dodecyl, 1,1,3,3,5,5-hexamethyl-hexyl, tridecyl, tetradecyl, pentadecyl, hexadecyl, heptadecyl, octadecyl, eicosyl, docosyl and tricosyl. One of the preferred meanings of  $R_5$ ,  $R_6$ ,  $R_{10}$ ,  $R_{12}$  and  $R_{13}$  is  $C_1-C_8$ alkyl, in particular methyl. One of the preferred meanings of  $R_3$  and  $R_6$  is  $C_1-C_2$ alkyl, in particular  $C_1-C_2$ alkyl, for example hexadecyl and  $C_{18}-C_{22}$ alkyl. One of the preferred meanings of  $R_6$  is  $C_1-C_2$ alkyl, in particular octadecyl.

[0021] Examples of  $C_5-C_{12}$ cycloalkyl are cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl and cyclohexadecyl.  $C_5-C_8$ cycloalkyl, in particular cyclohexyl, is preferred.

[0022] Examples of  $C_7-C_8$ phenylalkyl are benzyl and phenylmethyl.

[0023]  $C_7-C_8$ phenylalkyl which is substituted by  $C_1-C_8$ alkyl on the phenyl radical is, for example, methylbenzyl, dimethylbenzyl, trimethylbenzyl or tetra-butylbenzyl.

[0024] Examples of  $C_2-C_8$ alkenyl are allyl, 2-methylallyl, butenyl, pentenyl and hexenyl. Allyl is preferred.

[0025]  $C_1-C_8$ acyl is preferably  $C_1-C_8$ alkanoyl,  $C_3-C_6$ alkenoxy or benzoyl. Examples are formyl, acetyl, propionyl, butyryl, pentanoyl, hexanoyl, octanoyl, benzoyl, acryloyl and crotonoyl.

[0026] One of the preferred meanings of  $R_5$  and  $R_6$  is phenyl.

[0027]  $X_2$  and  $R_{12}$  are preferably a direct bond.

[0028]  $X_1$ ,  $X_2$ ,  $R_6$ ,  $R_{10}$  and  $R_{12}$  are preferably hydrogen.

[0029] The compounds described as components a) to c) are essentially known (in some cases commercially available) and can be prepared by known processes, for example as described in U.S. Pat. No. 4,233,412, U.S. Pat. No. 4,340,534, U.S. Pat. No. 4,857,595, DD-A-262 439 (Derwent 89-122 983/17, Chemical Abstracts 111 58 9649), DE-A-4 239 437 (Derwent 94-177 274/22), U.S. Pat. No. 4,529,760, U.S. Pat. No. 4,477,013 and Chemical Abstracts—CAS No. 136 504-96-6.

[0030] Component c) can be prepared analogously to known processes, for example by reaction of a polyamine of the formula VIa with cyanogen chloride in a molar ratio of from 1:2 to 1:4 in the presence of anhydrous lithium carbonate, sodium carbonate or potassium carbonate in an organic solvent, such as 1,2-dichloroethane, toluene, xylene,

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benzene, dioxane or tert-amyl alcohol, at a temperature of from -20°C. to +10°C., preferably from ~10°C. to +10°C., in particular from 0°C. to +10°C., for from 2 to 8 hours, followed by reaction of the resultant product with a 2,2,6,6-tetramethyl-4-piperidylamine of the formula VIb. The molar ratio between 2,2,6,6-tetramethyl-4-piperidylamine and polyamine of the formula VIa is, for example, from 4:1 to 8:1. The amount of 2,2,6,6-tetramethyl-4-piperidylamine can be added in one portion or in more than one portion at intervals of a few hours.

[0031] The poly(amine of the formula VIa)cyanuric chloride 2,2,6,6-tetramethyl-4-piperidylamine of the formula VIb ratio is preferably from 1:3.5 to 1:3.6

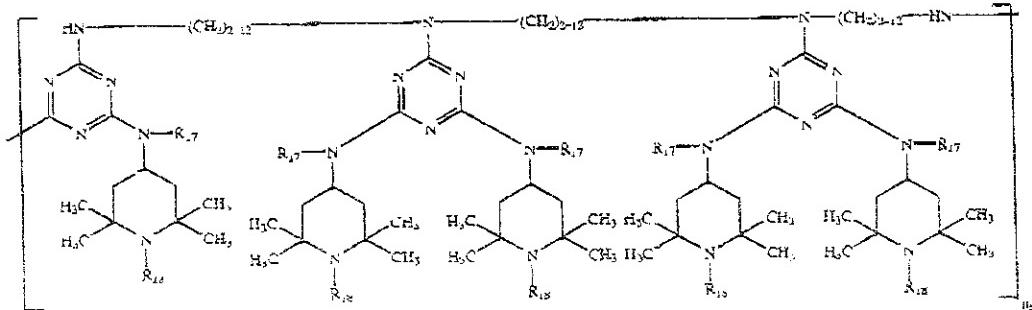
[0032] The following example indicates one way of preparing the preferred component c).

[0033] Example: 23.6 g (0.128 mol) of cyanuric chloride, 7.43 g (0.0426 mol) of N,N'-bis[3-aminopropyl]ethylenediamine and 18 g (0.13 mol) of anhydrous potassium carbonate are reacted at 5°C. for 3 hours with stirring in 250 mL

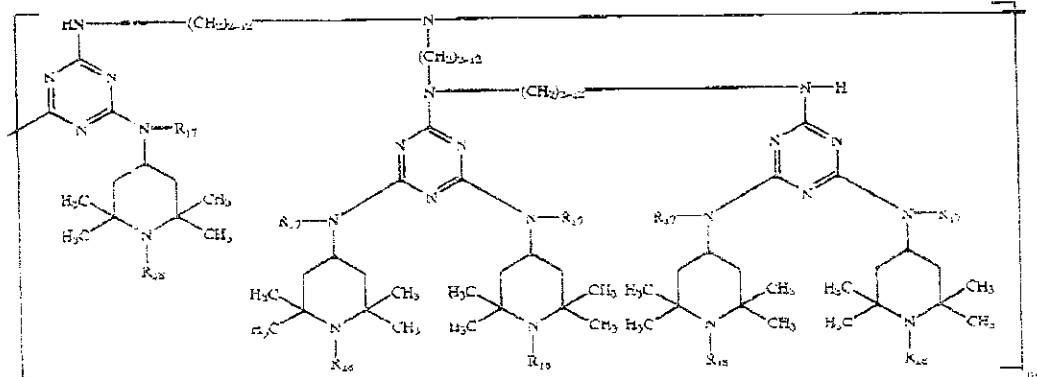
of 1,2-dichloroethane. The mixture is warmed at room temperature for a further 4 hours. 27.2 g (0.128 mol) of N-(2,2,6,6-tetramethyl-4-piperidyl)butylamine are added, and the resultant mixture is warmed at 60°C. for 3 hours. A further 15 g (0.13 mol) of anhydrous potassium carbonate are added, and the mixture is warmed at 60°C. for a further 6 hours. The solvent is removed by distillation under a slight vacuum (200 mbar) and replaced by xylene. 18.2 g (0.085 mol) of N-(2,2,6,6-tetramethyl-4-piperidyl)butylamine and 5.2 g (0.13 mol) of ground sodium hydroxide are added, the mixture is refluxed for 2 hours and the water formed during the reaction is removed by azeotropic distillation over a further 12 hours. The mixture is filtered. The solution is washed with water and dried over Na<sub>2</sub>SO<sub>4</sub>. The solvent is evaporated, and the residue is dried at 120-130°C. in vacuo (0.1 mbar). Component c) is obtained as a colourless resin.

[0034] In general, component c) can be represented for example by a compound of the formula VI-1, VI-2 or VI-3. It can also be in the form of a mixture of these three compounds.

(VI-1)



(VI-2)



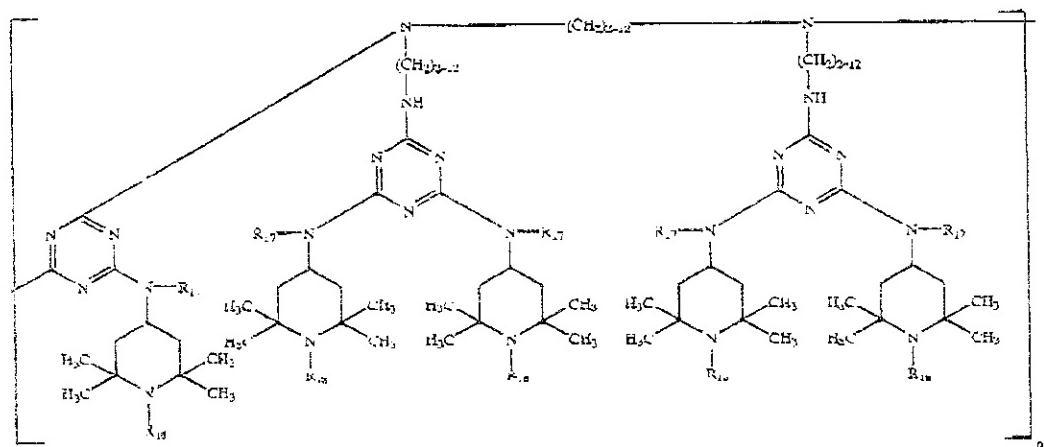
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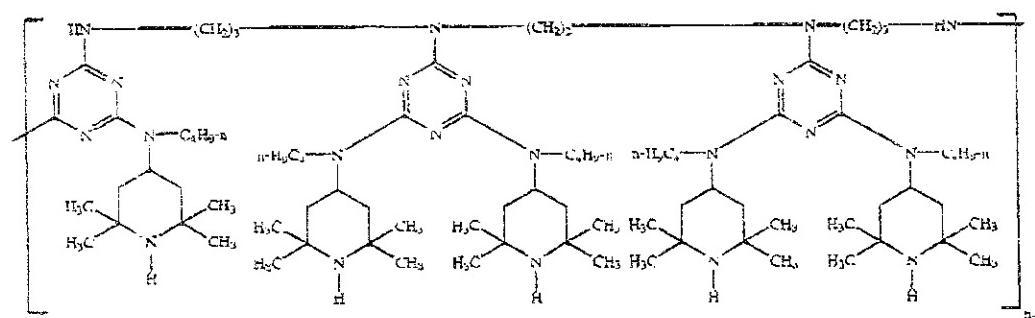
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(VII)



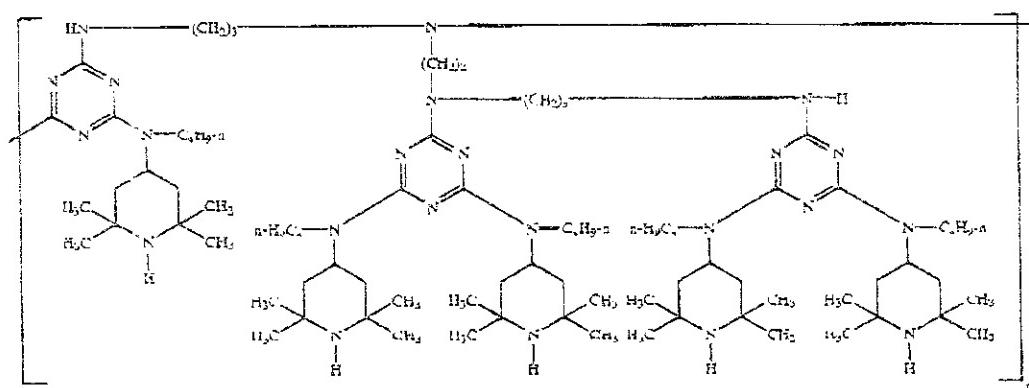
n5

A preferred meaning of the formula VII-1 is:



n2

A preferred meaning of the formula VII-2 is:



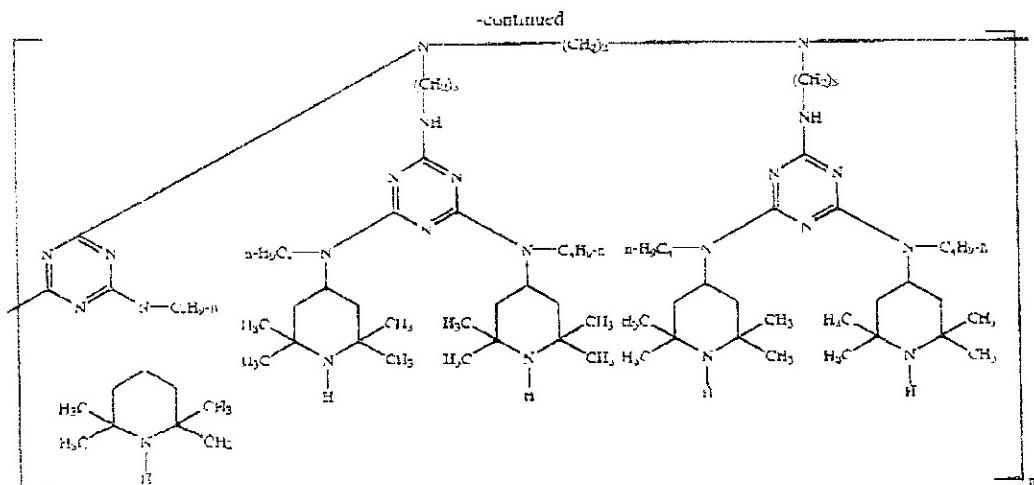
n5

A preferred meaning of the formula VII-3 is:

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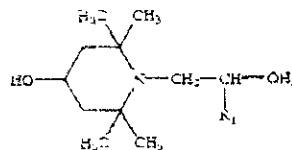
[0035] In the above formulae VI-1 to VI-3,  $n_3$  is preferably 1 to 20.

[0036] Component a) is preferably  $\circledcirc$ TINUVIN 622, component b) is preferably  $\circledcirc$ HOSTAVIN N 30, component c) is preferably  $\circledcirc$ UVINOL 5050 H,  $\circledcirc$ LICHTSCHUTZSTOFF UV 31 or  $\circledcirc$ LUCHEM B 18, component d) is preferably  $\circledcirc$ MARK LA 63 or  $\circledcirc$ MARK LA 68 and component e) is preferably  $\circledcirc$ UVASORB HA 88.

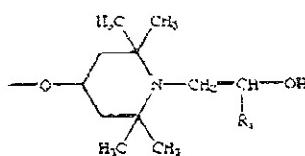
[0037] The compounds of the formulae IIa and IIb can be obtained together as a mixture and also employed as such as component b) in the novel stabilizer system. The IIa:IIb ratio is, for example, from 20:1 to 1:20 or from 1:10 to 10:1.

[0038] The meanings of the terminal groups which saturate the free valences in the compounds of the formulae I, IIa, IIb, III, IV, V, VI-1, VI-2 and VI-3 depend on the processes used for their preparation. The terminal groups can also be modified after the preparation of the compounds.

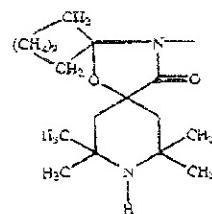
[0039] If the compounds of the formula I are prepared, for example, by reacting a compound of the formula



[0040] in which  $R_1$  is hydrogen or methyl, with a dicarboxylic acid anhydride of the formula  $Y-\text{OOC}-R_2-\text{COO}-Y$ , in which Y is, for example, methyl, ethyl or propyl, and  $R_2$  is as defined above, the terminal group bonded to the 2,2,6,6-tetramethyl-4-oxypiperidin-1-yl radical is hydrogen or  $-\text{C}(=\text{O})-\text{R}_3-\text{COO}-Y$ , and the terminal group bonded to the diaryl radical is  $-\text{O}-Y$  or



[0041] In the compounds of the formula IIa, the terminal group bonded to the nitrogen can be, for example, hydrogen and the terminal group bonded to the 2-hydroxypropylene radical can be, for example, a



[0042] group.

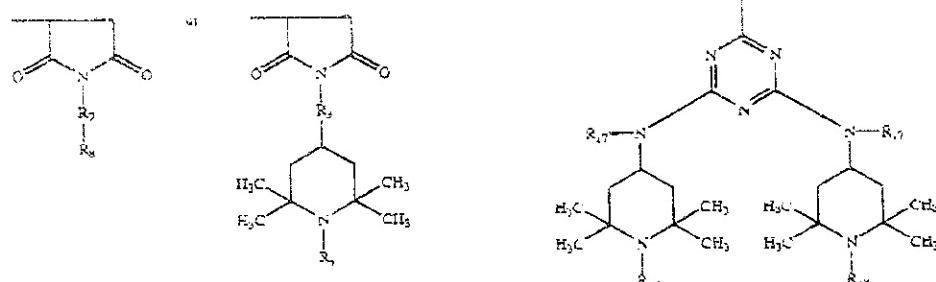
[0043] In the compounds of the formula IIb, the terminal group bonded to the dimethylene radical can be, for example,  $-\text{OH}$ , and the terminal group bonded to the oxygen can be, for example, hydrogen. The terminal groups can also be polyether radicals.

[0044] In the compounds of the formula III, the terminal group bonded to the 2,5-dioxopyrrolidine ring is, for example, hydrogen, and the terminal group bonded to the  $-\text{C}(\text{R}_5)(\text{R}_10)-$  radical is, for example,

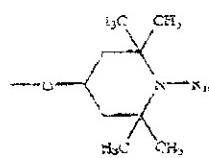
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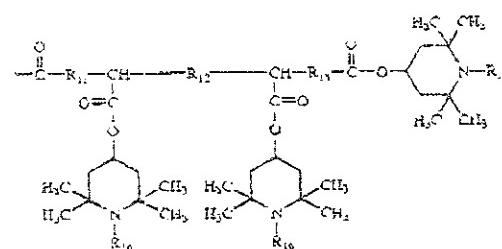
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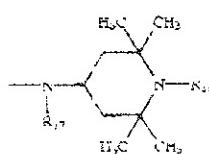
[0045] In the compounds of the formulae V, the terminal group bonded to the carbonyl radical is, for example,



[0046] and the terminal group bonded to the oxygen radical is, for example,



[0047] In the compounds of the formulae VI-1, VI-2 and VI-3, the terminal group bonded to the triazine radical is, for example, Cl or a



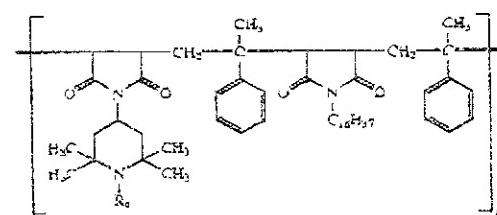
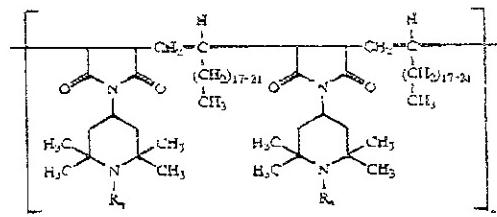
[0048] group, and the terminal group bonded to the amino radical is, for example, hydrogen or a

[0049] group

[0050] Preference is given to a stabilizer mixture in which R<sub>1</sub> is hydrogen, R<sub>2</sub> is ethylene, and n<sub>1</sub> is a number from 2 to 25

[0051] Preference is likewise given to a stabilizer mixture in which R<sub>3</sub> and R<sub>7</sub> are a direct bond or an —N(X<sub>1</sub>)—CO—X<sub>2</sub>—CO—N(X<sub>3</sub>)— group, where X<sub>1</sub> and X<sub>3</sub>, independently of one another, are hydrogen or C<sub>1</sub>-C<sub>4</sub> alkyl and X<sub>2</sub> is a direct bond, R<sub>4</sub> is hydrogen, C<sub>1</sub>-C<sub>4</sub> alkyl, OII, C<sub>6</sub>-C<sub>12</sub> alkoxy, C<sub>5</sub>-C<sub>9</sub>cycloalkoxy, allyl, benzyl or acetyl, R<sub>5</sub> and R<sub>6</sub> are C<sub>1</sub>-C<sub>2</sub>alkyl or phenyl, R<sub>6</sub> and R<sub>10</sub> are hydrogen or C<sub>1</sub>-C<sub>4</sub>alkyl, R<sub>8</sub> is C<sub>1</sub>-C<sub>2</sub>alkyl or a group of the formula IV, R<sub>11</sub>, R<sub>15</sub>, R<sub>16</sub> and R<sub>17</sub> are C<sub>1</sub>-C<sub>4</sub>alkylene, R<sub>12</sub> is a direct bond, and R<sub>13</sub> is as defined for R<sub>3</sub>.

[0052] Preference is also given to a stabilizer mixture in which component (c) is at least one compound of the formula:

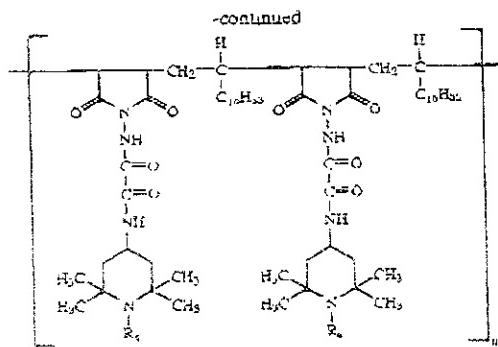


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[0053] in which R<sub>1</sub> is hydrogen or methyl, and n<sub>3</sub> is a number from 1 to 50

[0054] Component d) is preferably at least one compound of the formula

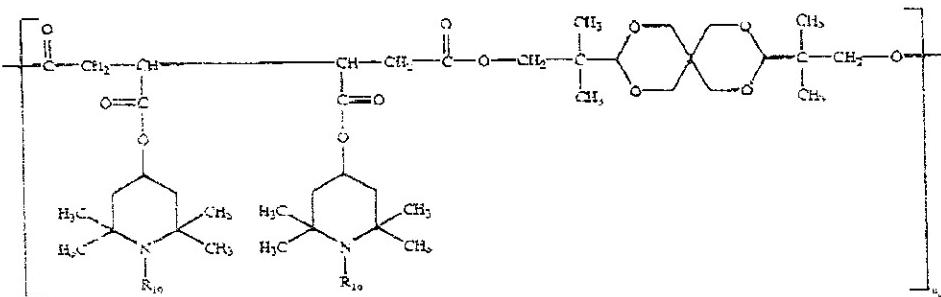
[0063] 5) stabilizer mixture comprising STINUVIN 622 and MARK LA 63,

[0064] 6) stabilizer mixture comprising STINUVIN 622 and UVASORB HA 98

[0065] 7) stabilizer mixture comprising STINUVIN 622 and UVASORB HA 98

[0066] The novel stabilizer mixture is suitable for stabilizing organic materials against thermal, oxidative or light-induced degradation. Examples of such materials are the following:

[0067] 1) Polymers of monoolefins and diolefins, for example polypropylene, polyisobutylene, polybut-1-ene, poly-4-methylpent-1-ene, polymuprene or polybutadiene, as well as polymers of cycloolefins, for instance of cyclopentene or norbornene, polyethylene (which optionally can be crosslinked), for example high density polyethylene (HDPE), high density and high molecular weight polyethylene (HDPE-HMW), high density and ultrahigh molecular weight polyethylene (HDPE-UHMW), medium density polyethylene (MDPE), low density polyethylene (LDPE),



[0055] in which R<sub>10</sub> is hydrogen or methyl, and n<sub>4</sub> is a number from 1 to 50

[0056] A stabilizer mixture comprising components a) and b) is preferred. Likewise preferred is a stabilizer mixture comprising components a) and c) and a stabilizer mixture comprising components a) and d). Particular preference is given to a stabilizer mixture comprising components a) and c).

[0057] n<sub>1</sub> is preferably from 5 to 20, n<sub>2</sub> and n<sub>2'</sub> are preferably from 2 to 10, and n<sub>3</sub>, n<sub>4</sub> and n<sub>5</sub> are preferably from 1 to 10.

[0058] The following stabilizer systems are particularly preferred embodiments of the invention

[0059] 1) stabilizer mixture comprising STINUVIN 622 and HOSTAVIN N 30,

[0060] 2) stabilizer mixture comprising STINUVIN 622 and UVINUL 5050 H,

[0061] 3) stabilizer mixture comprising STINUVIN 622 and GLICHTSCHUTZSTOFF UV 31,

[0062] 4) stabilizer mixture comprising STINUVIN 622 and GLUCHEM B 18,

linear low density polyethylene (LLDPE), branched low density polyethylene (BLDPE)

[0068] Polyolefins, i.e. the polymers of monoolefins exemplified in the preceding paragraph, preferably polyethylene and polypropylene, can be prepared by different, and especially by the following, methods

[0069] a) radical polymerisation (normally under high pressure and at elevated temperature)

[0070] b) catalytic polymerisation using a catalyst that normally contains one or more than one metal of groups IVB, VB, VIB or VIII of the Periodic Table. These metals usually have one or more than one ligand, typically oxides, halides, alkoholates, esters, ethers, amides, alkyls, alkynyls and/or aryls that may be either π- or σ-coordinated. These metal complexes may be in the free form or fixed on substrates, typically on activated magnesium chloride, titanium(III) chloride, alumina or silicon oxide. These catalysts may be soluble or insoluble in the polymerisation medium. The catalysts can be used by themselves in the polymerisation or further activators may be used, typically metal alkyls, metal

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hydrides, metal alkyl halides, metal alkyl oxides or metal alkyl oxanes, said metals being elements of groups Ia, IIa and/or IIIa of the Periodic Table. The activators may be modified conveniently with further ester, ether, amine or vinyl ether groups. These catalyst systems are usually termed Phillips, Standard Oil Indiana, Ziegler (-Natta), TNZ (DuPont), metallocene or single site catalysts (SSC).

[0071] 2 Mixtures of the polymers mentioned under 1), for example mixtures of polypropylene with polyisobutylene, polypropylene with polyethylene (for example PP/HDPE, PP/LDPE) and mixtures of different types of polyethylene (for example LDPE/HDPE).

[0072] 3. Copolymers of monoolefins and diolefins with each other or with other vinyl monomers, for example ethylene/propylene copolymers, linear low density polyethylene (LLDPE) and mixtures thereof with low density polyethylene (LDPE), propylene/butyl-1-one copolymers, propylene/isobutylene copolymers, ethylene/butyl- $\alpha$ -methylpenylene copolymers, ethylene/heptene copolymers, ethylene/methylpenylene copolymers, ethylene/heptene copolymers, propylene/butadiene copolymers, isobutylene/isoprene copolymers, ethylene/alkyl acrylate copolymers, ethylene/alkyl methacrylate copolymers, ethylene/vinyl acetate copolymers and their copolymers with carbon monoxide or ethylene/acrylic acid copolymers and their salts (monomers) as well as terpolymers of ethylene with propylene and a diene such as hexadiene, dicyclopentadiene or ethylidene-norbornene, and mixtures of such copolymers with one another and with polymers mentioned in 1) above, for example polypropylene/ethylene-propylene copolymers, LDPE/ethylene-vinyl acetate copolymers (EVA), LDPE/ethylene-acrylic acid copolymers (EAA), LDPE/EVA, LDPE/EAA and alternating or random polyalkylene/carbon monoxide copolymers and mixtures thereof with other polymers, for example polyamides.

[0073] 4 Hydrocarbon resins (for example C<sub>5</sub>-C<sub>9</sub>) including hydrogenated modifications thereof (e.g. tackifiers) and mixtures of polyalkylenes and starch.

[0074] 5. Polystyrene, poly(p-methylstyrene), poly( $\alpha$ -methylstyrene).

[0075] 6. Copolymers of styrene or  $\alpha$ -methylstyrene with dienes or acrylate derivatives, for example styrene/butadiene, styrene/styrene oxide, styrene/alkyl methacrylate, styrene/butadiene/alkyl acrylate, styrene/butadiene/alkyl methacrylate, styrene/maleic anhydride, styrene/acrylonitrile/methyl acrylate, mixtures of high impact strength of styrene copolymers and another polymer, for example a polycarbonate, a diene polymer or an ethylene/propylene/diene terpolymer, and block copolymers of styrene such as styrene/butadiene/styrene, styrene/propene/styrene, styrene/ethylene/butylene/styrene or styrene/ethylene/propylene/styrene.

[0076] 7 Graft copolymers of styrene or  $\alpha$ -methylstyrene, for example styrene on polybutadiene, styrene on polybutadiene-styrene or polybutadiene-acrylonitrile copolymers; styrene and acrylonitrile (or methacrylonitrile) on polybutadiene, styrene, acrylonitrile and methyl methacrylate on polybutadiene, styrene and maleic anhydride or maleimide on polybutadiene; styrene and maleimide on polybutadiene; styrene and alkyl acrylates or methacrylates on

polybutadiene; styrene and acrylonitrile on ethylene/propylene/diene terpolymers; styrene and acrylonitrile on polyalkyl acrylates or polyalkyl methacrylates, styrene and acrylonitrile on acrylate/butadiene copolymer, as well as mixtures thereof with the copolymers listed under 6), for example the copolymer mixtures known as ABS, MBS, ASA or AES polymers.

[0077] 8 Halogen-containing polymers such as polychloropropene, chlorinated rubbers, chlorinated and brominated copolymer of isobutylene-isoprene (halobutyl rubber), chlorinated or sulfochlorinated polyethylene, copolymers of ethylene and chlorinated ethylene, epichlorohydrin homopolymer and copolymers, especially polymers of halogen-containing vinyl compounds, for example polyvinyl chloride, polyvinylidene chloride, polyvinyl fluoride, polyvinylidene fluoride, as well as copolymers thereof such as vinyl chloride/vinylidene chloride, vinyl chloride/vinyl acetate or vinylidene chloride/vinyl acetate copolymers.

[0078] 9 Polymers derived from  $\alpha,\beta$ -unsaturated acids and derivatives thereof such as polyacrylates and polymethacrylates, polymethyl methacrylates, polyacrylamides and polyacryonitriles, impact-modified with butyl acrylate.

[0079] 10. Copolymers of the monomers mentioned under 9) with each other or with other unsaturated monomers, for example acrylonitrile/butadiene copolymers, acrylonitrile/alkyl acrylate copolymers, acrylonitrile/alkoxyalkyl acrylate or acrylonitrile/vinyl halide copolymers or acrylonitrile/alkyl methacrylate/butadiene terpolymers.

[0080] 11. Polymers derived from unsaturated alcohols and amines or the acyl derivatives or salts thereof, for example polyvinyl alcohol, polyvinyl acetate, polyvinyl stearate, polyvinyl benzoate, polyvinyl maleate, polyvinyl butyral, polyallyl phthalate or polyallyl melamine, as well as their copolymers with olefins mentioned in 1) above.

[0081] 12 Homopolymers and copolymers of cyclic ethers such as polyisopylene glycols, polyethylene oxide, polypropylene oxide or copolymers thereof with bisglycidyl ethers.

[0082] 13 Polyacetals such as polyoxymethylene and those polyoxymethylene which contain ethylene oxide as a comonomer, polyacetals modified with thermoplastic polyurethane, acrylates or MBS.

[0083] 14. Polyphenylene oxides and sulfides, and mixtures of polyphenylene oxides with styrene polymers or polyamides.

[0084] 15 Polyurethanes derived from hydroxyl-terminated polyesters, polyesters or polybutadienes on the one hand and aliphatic or aromatic polyisocyanates on the other, as well as precursors thereof.

[0085] 16. Polyamides and copolyamides derived from diamines and dicarboxylic acids and/or from aminocarboxylic acids or the corresponding lactams, for example polyamide 4, polyamide 6, polyamide 6/6, 6/10, 6/9, 6/12, 4/6, 12/12, polyamide 11, polyamide 12, aromatic polyamides starting from m-xylylene diamine and adipic acid; polyamides prepared from hexamethylene diamine and isophthalic or/and terephthalic acid and with or without an elastomer as modifier, for example poly-2,4,4,-trimethylhexamethylene terephthalamide or poly-m-phenylene isophthalamide; and also block copolymers of the aforementioned polyamides.

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with polyolefins, olefin copolymers, ionomers or chemically bonded or grafted elastomers, or with polyethers, e.g. with polycyclic glycol, polypropylene glycol or polyisobutylene glycol, as well as polyamides or copolyamides modified with EPDM or ABS; and polyamides condensed during processing (RIM polyamide systems)

[0086] 17. Polyureas, polyimides, polyamide-imides, polyetherimides, polyestersimides, polyhydantoin and polybenzimidazoles.

[0087] 18. Polyesters derived from dicarboxylic acids and diols and/or from hydroxycarboxylic acids or the corresponding lactones, for example polyethylene terephthalate, polybutylene terephthalate, poly-1,4-dimethylcyclohexane terephthalate and polyhydroxybutyrate, as well as block copolyesters derived from hydroxyl-terminated polyethers; and also polyesters modified with polycarbonates or MBS.

[0088] 19. Polycarbonates and polyesters carbonates

[0089] 20. Polysulfones, polyether sulfones and polyether ketones

[0090] 21. Crosslinked polymers derived from aldehydes on the one hand and phenols, ureas and melamines on the other hand, such as phenol/formaldehyde resins, urea/formaldehyde resins and melamine/formaldehyde resins

[0091] 22. Drying and non-drying alkyl resins.

[0092] 23. Unsaturated polyester resins derived from copolymers of saturated and unsaturated dicarboxylic acids with polyhydroxyl alcohols and vinyl compounds as crosslinking agents, and also halogen-containing modifications thereof of low flammability

[0093] 24. Crosslinkable acrylic resins derived from substituted acrylates, for example epoxy acrylates, urethane acrylates or polyester acrylates

[0094] 25. Alkyd resins, polyester resins and acrylic resins crosslinked with melamine resins, urea resins, isocyanates, isocyanurates, polyisocyanates or epoxy resins

[0095] 26. Crosslinked epoxy resins derived from aliphatic, cyclosiliphatic, heterocyclic or aromatic glycidyl compounds, e.g. products of diglycidyl ethers of bisphenol A and bisphenol E, which are crosslinked with customary hardeners such as anhydrides or amines, with or without accelerators.

[0096] 27. Natural polymers such as cellulose, rubber, gelatin and chemically modified homologous derivatives thereof, for example cellulose acetates, cellulose propionate and cellulose butyrate, or the cellulose ethers such as methyl cellulose, as well as rosins and their derivatives.

[0097] 28. Blends of the aforementioned polymers (poly-blends), for example PP/EPDM, Polyamide/EPDM or ABS, PVC/EVA, PVC/ABS, PVC/MBS, PC/ABS, PB1P/ABS, PC/ASA, PC/PBT, PVC/CPE, PVC/acrylates, POM/thermoplastic PUR, PC/thermoplastic PUR, POM/acrylate, POM/MBS, PPO/HIPS, PPO/PA 6,6 and copolymers, PA/HDPE, PA/PP, PA/PPO, PB1/PC/ABS or PBT/PET/PC.

[0098] 29. Naturally occurring and synthetic organic materials which are pure monomeric compounds or mixtures of such compounds, for example mineral oils, animal and vegetable fats, oil and waxes, or oils, fats and waxes based

on synthetic esters (e.g. pivalates, adipates, phosphates or trimellitates) and also mixtures of synthetic esters with mineral oils in any weight ratios, typically those used as spinning compositions, as well as aqueous emulsions of such materials.

[0099] 30. Aqueous emulsions of natural or synthetic rubber, e.g. natural latex or latexes of carboxylated styrene/butadiene copolymers.

[0100] The invention therefore furthermore relates to a composition comprising an organic material which is sensitive to oxidative, thermal or light-induced degradation and a novel stabilizer mixture.

[0101] The organic material is preferably a synthetic polymer, in particular from one of the above groups. Polyolefins are preferred, and polyethylene, polypropylene and copolymers thereof are particularly preferred.

[0102] The components of the novel stabilizer system can be added to the material to be stabilized either individually or mixed with one another. The components can be employed, independently of one another, in amounts of from 0.01 to 4.99%, with the proviso that the total amount of component a) and component b), c), d) or e) is from 0.02 to 5%, based on the total weight of the material to be stabilized.

[0103] The total amount of component a) and component b), c), d) or e) is preferably from 0.05 to 3%, in particular from 0.05 to 2%, or from 0.05 to 1%, based on the total weight of the material to be stabilized.

[0104] The weight ratio between component a) and component b), c), d) or e) is preferably from 20:1 to 1:20, in particular from 10:1 to 1:10, for example from 5:1 to 1:5.

[0105] The novel stabilizer mixture or the individual components thereof can be incorporated into the organic material by known methods, for example before or during shaping or by applying the dissolved or dispersed compounds to the organic material, if necessary with subsequent evaporation of the solvent. The individual components of the novel stabilizer mixture can be added to the materials to be stabilized in the form of a powder, granules or a masterbatch, which contains these components in, for example, a concentration of from 2.5 to 25% by weight.

[0106] If desired, the components of the novel stabilizer system can be melt blended with one another before incorporation in the organic material.

[0107] The novel stabilizer system or its components can be added before or during the polymerization or before the crosslinking.

[0108] The materials stabilized in this way can be used in a wide variety of forms, for example as films, fibres, tapes, moulding compositions, profiles or as binders for paints, adhesives or putties.

[0109] The stabilized organic materials of the invention may additionally also contain various conventional additives, for example:

[0110] 1. Antioxidants

[0111] 1.1. Alkylated monophenols, for example 2,6-di-tert-butyl-4-methylphenol, 2-tert-butyl-4,6-dimethylphenol, 2,6-di-tert-butyl-4-ethoxyphenol, 2,6-di-tert-butyl-4-n-butylophenol, 2,6-di-tert-butyl-4-isobutylphenol, 2,6-dicyclo-

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pcaryl-4-methylphenol, 2-( $\alpha$ -methylcyclohexyl)-4,6-dimethylphenol, 2,6-diisooctadecyl-4-methylphenol, 2,6-di-tert-butyl-4-methoxybenzyl phenol, novarylphenols which are linear or branched in the side chains, for example, 2,6-di-nonyl-4-methylphenol, 2,4-dimethyl-6-(1-methylundec-1-yl)phenol, 2,4-dimethyl-6-(1-methylheptadec-1-yl)phenol, 2,4-dimethyl-6-(1-methylundec-1-yl)phenol and mixtures thereof.

[0112] 1.2 Alkylihomethylphenols, for example 2,4-dioctylhomethyl- $\alpha$ -tert-butylphenol, 2,4-dioctylhomethyl-6-methylphenol, 2,4-dioctylhomethyl- $\alpha$ -ethylphenol, 2,6-diisooctadecylhomethyl-4-nonylphenol

[0113] 1.3. Hydroquinones and alkylated hydroquinones, for example 2,6-di-tert-butyl methoxyphenol, 2,5-di-tert-butylhydroquinone, 2,5-di-tert-amylhydroquinone, 2,6-di-phenyl-4-octadecyloxyphenol, 2,6-di-tert-butylhydroquinone, 2,5-di-tert-butyl 4-hydroxy-anisole, 3,5-di-tert-butyl-4-hydroxyanisole, 3,5-di-tert-butyl-4-hydroxyphenylsucinate, bis(3,5-di-tert-butyl-4-hydroxyphenyl)sulfate.

[0114] 1.4 Tocopherols, for example  $\alpha$ -tocopherol,  $\beta$ -tocopherol,  $\gamma$ -tocopherol,  $\delta$ -tocopherol and mixtures thereof (Vitamin E).

[0115] 1.5. Hydroxylated thiociphenyl ethers, for example 2,2'-thiobis(6-tert-butyl-4-methylphenol), 2,2'-thiobis(4- $\alpha$ -cetylphenol), 4,4'-thiobis(6-tert-butyl-3-methylphenol), 4,4'-thiobis(6-tert-butyl-2-methylphenol), 4,4'-thiobis(3,6-disubstitutedphenol), 4,4'-bis(2,6-dimethyl-4-hydroxyphenyl)disulfide

[0116] 1.6 Alkylidenediphenols, for example 2,2'-methylenebis(6-tert-butyl-4-methylphenol), 2,2'-methylenebis(6-tert-butyl-4- $\alpha$ -methylphenol), 2,2'-methylenebis[4-methyl-5-( $\alpha$ -methylcyclohexyl)phenol], 2,2'-methylenecis(3-methyl-6-cyclohexylphenol), 2,2'-methylenecis(6- $\alpha$ -methyl-4-methylphenol), 2,2'-methylenecis(4,6-di-tert-butylphenol), 2,2'-ethylenecis(4,6-di-tert-butylphenol), 2,2'-ethylenecis(6-tert-butyl-4-hydroxyphenol), 2,2'-methylenecis[6-( $\alpha$ , $\omega$ -dimethylbenzyl)-4-nonylphenol], 4,4'-methylenebis(2,6-di-tert-butylphenol), 4,4'-methylenecis(6-tert-butyl-2-methylphenol), 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)triazo, 2,6-bis(3-tert-butyl-5-methyl-2-hydroxybenzyl)-4-methylphenol, 1,1-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)buranate, 1,1-bis(5-tert-butyl-4-hydroxy-2-methyl-phenyl)-3-n-dodecylmercaptobutane, ethylene glycol bis[3,3-bis(3'-4-tert-butyl-4-hydroxyphenyl)dipropylate], bis(3-tert-butyl-4-hydroxy-5-methyl-phenyl)dicyclohexadiene, bis[2-(3-tert-butyl-2-hydroxy-5-methylbenzyl)-6-tert-butyl-4-methylphenyl]ketophthalate, 1,1-bis(3,5-dimethyl-2-hydroxyphenyl)buranate, 2,2-bis(3,5-di-tert-butyl-4-hydroxyphenyl)propane, 2,2-bis(5-tert-butyl-4-hydroxy-2-methylphenyl)-4-hydroxybutylmercaptobutane, 1,1,5-tris(5-tert-butyl-4-hydroxy-2-methylphenyl)pentane

[0117] 1.7. O-, N- and S-benzyl compounds, for example 3,5,3'-5'-tetra- $\alpha$ -tert-butyl-4,4'-dihydroxydibenzoylether, octadecyl-4-hydroxy-3,5-dimethylbenzylmercaptoacetate, 16-decyl-4-hydroxy-3,5-di-tert-butylbenzylmercaptoacetate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)-amine, bis(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl) dihydroterephthalate, bis(3,5-di-tert-butyl-4-hydroxybenzyl)sulfide, isoctyl-3,5-di-tert-butyl-4-hydroxybenzylmercaptoacetate.

[0118] 1.8 Hydroxybenzylated malonates, for example dioctadecyl-2,2-bis(3,5-di-tert-butyl-2-hydroxybenzoyl)-

malonate, di-octadecyl-2-(3-tert-butyl-4-hydroxy-5-methylbenzyl)-malonate, di-octadecylmercaptoethyl-2,2-bis(3,5-di-tert-butylhydroxybenzyl)malonate, bis[4-(1,1,3,3-tetramethylbutyl)phenyl]-2,2-bis(3,5-di-tert-butylhydroxybenzyl)malonate

[0119] 1.9 Aromatic hydroxybenzyl compounds, for example 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)-2,4,6-trimethylbenzene, 1,4-bis(3,5-di-tert-butyl-4-hydroxybenzyl)-2,3,5,6-tetramethylbenzene, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxybenzyl)phenol.

[0120] 1.10 Triazine Compounds, for example 2,4-bis(octylmercapto)-6-(3,5-di-tert-butyl-4-hydroxyandino)-1,3,5-triazine, 2-octylmercapto-5,6-bis(3,5-di-tert-butyl-4-hydroxyallino)-1,3,5-triazine, 2-octylmercapto-4,6-dis(3,5-di-tert-butyl-4-hydroxyphenoxo)-1,3,5-triazine, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenoxo)-1,2,3-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxybenzyl)succinamate, 1,3,5-tris(4-tert-butyl-3-hydroxy-2,6-dimethylbenzyl)succinamate, 2,4,6-tris(3,5-di-tert-butyl-4-hydroxyphenylthiobutyl)-1,3,5-triazine, 1,3,5-tris(3,5-di-tert-butyl-4-hydroxypropionyl)-hexahydro-1,3,5-triazine, 1,3,5-tris(3,5-dicyclohexyl-4-hydroxybenzyl)succinamate.

[0121] 1.11 Benzylphosphonates, for example dimethyl-2,5-di-tert-butyl-4-hydroxybenzylphosphonate, diethyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-3,5-di-tert-butyl-4-hydroxybenzylphosphonate, dioctadecyl-5-tert-butyl-4-hydroxy-3-methylbenzyl-phosphonate, the calcium salt of the monoester of 3,5-di-tert-butyl-4-hydroxybenzyl-phosphonic acid.

[0122] 1.12. Acylamino phenols, for example 4-hydroxy-lauramide, 4-hydroxysarcosamide, octyl N-(3,5-di-tert-butyl-4-hydroxyphenyl)carbamate.

[0123] 1.13. Esters of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)proprionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, undecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, triethylene glycol, diethylene glycol, triethylene glycol, pentacyrthritol, tris(hydroxyethyl)isocyanurate, N,N-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethyl-hexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospho-2,6,7-trioxabicyclo[2.2.2]octane.

[0124] 1.14 Esters of  $\beta$ -(5-tert-butyl-4-hydroxy-3-methylphenyl)proprionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, n-octanol, i-octanol, octadecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentacyrthritol, tris(hydroxyethyl)isocyanurate, N,N-bis(hydroxyethyl)oxamide, 3-thiaundecanol, 3-thiapentadecanol, trimethylolpropane, 4-hydroxymethyl-1-phospho-2,6,7-trioxabicyclo[2.2.2]octane.

[0125] 1.15. Esters of  $\beta$ -(3,5-dicyclohexyl-4-hydroxyphenyl)proprionic acid with mono- or polyhydric alcohols, e.g. with methanol, ethanol, octanol, undecanol, 1,6-hexanediol, 1,9-nonanediol, ethylene glycol, 1,2-propanediol, neopentyl glycol, thiodiethylene glycol, diethylene glycol, triethylene glycol, pentacyrthritol, tris(hydroxyethyl)isocyanurate, N,N-bis(hydroxyethyl)oxamide, 3-thiaundecanol, trimethylolhexanediol, trimethylolpropane, 4-hydroxymethyl-1-phospho-2,6,7-trioxabicyclo[2.2.2]octane.

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[0126] 1.16. Esters of 3,5-di-tert-butyl-4-hydroxyphenyl acetic acid with mono- or polyhydrox alcohols, e.g. with methanol, ethanol, octanol, octadecanol, 1,6-hexamethyl, 1,9-nonadecanol, vinylene glycol, 1,2-propanediol, acetyl glycol, triisobutylene glycol, diethylene glycol, methylene glycol, pentene glycol, bis(2-hydroxyethyl)isocyanurate, N,N'-bis(hydroxyethyl)oxamic, 3-hexadecanol, 3-hydroxyoctadecanol, vinylidhexadecanol, tri-methylolpropionate, 4-hydroxymethyl-1-phospho-2,6,7-trioxapencyclo[2.2.2]octane.

[0127] 1.17. Amides of  $\beta$ -(3,5-di-tert-butyl-4-hydroxyphenyl)propiionic acid e.g. N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hexadecylendiamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)trimethyl endiamine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenylpropionyl)hydrazine

[0128] 1.18. Ascorbic acid (vitamin C)

[0129] 1.19. Aromatic amine dianimes, for example N,N'-diisopropyl-p-phenylenediamine, N,N'-di-tert-butyl-p-phenylenediamine, N,N'-bis(1,4-dimethylpentyl)-p-phenylenediamine, N,N'-bis(1-ethyl-3-methylpentyl)-p-phenylenediamine, N,N'-bis(1-ethylhexyl)-p-phenylenediamine, N,N'-dicyclononyl-p-phenylenediamine, N,N'-diphenyl-p-phenylenediamine, N,N'-bis(2-naphthyl)-p-phenylenediamine, N-isopropyl-N'-phenyl-p-phenylenediamine, N-(1,3-dimethylbutyl)-N'-phenyl-p-phenylenediamine, N-(1-methylethyl)-N'-phenyl-p-phenylenediamine, N-cyclohexyl-N'-phenyl-p-phenylenediamine, 4-(p-toluenesulfonyl)-diphenylamine, N,N'-dimethyl-N,N'-di-tert-butyl-p-phenylenediamine, diphenylamine, N-allyldiphenylamine, 4-isopropoxydiphenylamine, N-phenyl-1-naphthylamine, N-(4-tert-octylphenyl)-1-naphthylamine, N-phenyl-2-naphthylamine, octylated diphenylamine, for example p,p'-di-tert-octyldiphenylamine, 4-n-butylamino phenol, 4-butylaminophenol, 4-nonaloylamino-phenol, 4-dodecanoylaminophenol, 4-undecanoylamino-phenol, bis(4methoxyphenyl)amine, 2,6-di-tert-butyl4dimethylaminomethyl phenol, 2,4-diaminodiphenylmethane, 4,4-diaminodiphenylmethane, N,N,N',N'-tetramethyl-4,4'-diaminodiphenylmethane, 1,2-bis(2-methylphenyl)aminoethane, 1,2-bis(phenylamino)propane, (o-tolyloxy)guanidine, Bis[4-(1,3-dimethylbutyl)-phenyl]amine, tert-octylated N-phenyl-1-naphthylamine, a mixture of mono- and diarylated tert-butyl/tert-octylphenyl-amines, a mixture of mono- and diarylated nonylidiphenylamines, a mixture of mono- and diarylated octadecylidiphenylamines, a mixture of mono- and diarylated isooctyloxyidiphenylamines, a mixture of mono- and diarylated tert-butylidiphenylamines, 2,3-dihydro-3,3-dimethyl-4H-1,4-dioxothiazine, phenothiazine, a mixture of mono- and diarylated tert-octylidiphenylamines, a mixture of mono- and diarylated tert-octyphenothiazines, N-allylphenothiazin, N,N,N',N'-tetra-tert-butyl-1,4-diaminobut-2-ene, N,N'-bis (2,2,6,6-tetramethyl-piperid-4-yl)-N-allylmethylenediamine, bis(2,2,6,6-tetra-methylpiperid-4-yl)succinate, 2,2,6,6-tetramethylpiperidin-4-one, 2,2,6,6-tetramethylpiperidin-4-ol

[0130] 2 UV Absorber and Light Stabilisers

[0131] 2.1 2-(2-Hydroxyphenyl)benzotriazoles, for example 2-(2-hydroxy-5-methylphenyl)benzotriazole, 2-(3,5-di-tert-butyl-2-hydroxyphenyl)benzotriazole, 2-(2-hydroxy-4-oxycarbonylphenyl)benzotriazole, 2-(3,5-di-( $\alpha,\alpha$ -dimethylbenzyl)-2-hydroxyphenyl)benzotriazole, mixture of 2-(3-tert-butyl-2-hydroxy-5-(2-oxy-carbonylphenyl)-5-chloro-benzotriazole, 2-(3-tert-butyl-5-[2-(2-ethylhexyloxy)-carbonylphenyl]-5-chloro-benzotriazole, 2-(3-tert-butyl-2-hydroxy-5-(2-methoxycarbonylphenyl)phenyl)-5-chloro-benzotriazole, 2-(3-tert-butyl-2-hydroxy-5-(2-octyloxy carbonylphenyl)phenyl)benzotriazole, 2-(3-tert-butyl-5-[2-(2-ethylhexyloxy)carbonyl-ethyl]-2-hydroxyphenyl)benzotriazole, 2-(3-dodecyl-2-hydroxy-5-methylphenyl)benzotriazole, and 2-(3-tert-butyl-2-hydroxy-5-(2-isooctyloxy carbonylphenyl)phenyl)benzotriazole, 2,2-methylene-dis[4(1,1,3,3-tetramethylbutyl)-6-benzotriazole-2-ylphenol], the transesterification product of 2-(3-tert-butyl-5-(2-methoxycarbonylphenyl)-2-hydroxyphenyl)-2H-benzotriazole with polyethylene glycol 300; [R-CH<sub>2</sub>CH<sub>2</sub>-COO(CH<sub>2</sub>)<sub>n</sub>], where R=3-tert-butyl-4-hydroxy-5'-2H-benzotriazole-2-ylphenyl.

[0132] 2.2 2-Hydroxybenzophenones, for example the 4-hydroxy, 4-methoxy, 4-octyloxy, 4-decyloxy, 4-dodecyloxy, 4-benzoyloxy, 4,4'-trihydroxy and 2-hydroxy-4,4'-dimethoxy derivatives.

[0133] 2.3. Esters of substituted and unsubstituted benzic acids, as for example 4-tert-butylphenyl salicylate, phenyl salicylate, octylphenyl salicylate, dibenzoyl resorcinol, bis(4-tert-butylbenzoyl) resorcinol, benzoyl resorcinol, 2,4-di-tert-butylphenyl 3,5-di-tert-butyl- $\rightarrow$ hydroxybenzoate, hexadecyl 3,5-di-tert-butyl-4-hydroxybenzoate, octadecyl 3,5-di-tert-butyl-4hydroxybenzoate, 2-methyl-4,6-di-tert-butylphenyl 3,5-di-tert-butyl-4-hydroxybenzoate.

[0134] 2.4 Acrylates, for example ethyl  $\alpha$ -cyano- $\beta$ -diphenylacrylate, isooctyl  $\alpha$ -cyano- $\beta$ -diphenylacrylate, methyl  $\alpha$ -carbomethoxy- $\beta$ -methyl- $\alpha$ -methoxy- $\beta$ -methyl- $\alpha$ -methoxy- $\beta$ -methyl- $\alpha$ -carbomethoxy- $\beta$ -methyl- $\alpha$ -methoxy- $\beta$ -methyl- $\alpha$ -carbomethoxy- $\beta$ -methyl- $\alpha$ -carbomethoxy- $\beta$ -methyl- $\alpha$ -carbomethoxy- $\beta$ -methyl-2-methylindoline

[0135] 2.5. Nickel compounds, for example nickel complexes of 2,2-thiobis-[4(1,1,3,3-tetramethylbutyl)phenol], such as the 1:1 or 1:2 complex, with or without additional ligands such as n-butylamine, triethanolamine or N- $\alpha$ -hydroxyethylmethanamine, nickel dibutylthiocarbamate, nickel salts of the monoalkyl esters, e.g. the methyl or ethyl ester, of 4-hydroxy-3,5-di-tert-butylbenzylphosphonic acid, nickel complexes of boroximes, e.g. of 2-hydroxy-4-methylphenyl undecylboroxime, nickel complexes of 1-phenyl-tauro-5-hydroxypyrazole, with or without additional ligands

[0136] 2.6 Sterically hindered amines, for example bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)succinate, bis(1-octyloxy-2,2,6,6-tetramethyl-4-piperidyl)succinate, bis(1,2,2,6,6-pentamethyl-4-piperidyl)bis(1-3,5-di-tert-butyl-4-hydroxybenzylmalonate), the condensate of 1-(2-hydroxyethyl)-2,2,6,6-tetramethyl-4-hydroxypiperidine and succinic acid, the condensate of N,N-

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dis(2,2,6,6-tetramethyl-4-piperidyl)hexaamethylene diamine and 4-tert-octyl amine-2,6-dichloro-1,3,5-triazine, bis(2,2,6,6-tetramethyl-4-piperidyl)dinitrouracile, tetrakis(2,2,6,6-tetramethyl-4-piperidyl)-1,2,3,4-butanetetracarboxylate, 1,1'-(1,2-ethane-diyl)bis(3,3,5,5-tetramethyl(piperazinone)), 4-benzoyl-2,2,6,6-tetramethylpiperidine, 4-stearylxylo-2,2,6,6-tetramethylpiperidine, bis(1,2,2,6,6-pentamethyl(piperidyl)-2-n-butyl-2-(2-hydroxy-3,5-di-tert-butylbenzyl)malonate, 3-*n*-octyl-7,7,9,9-tetramethyl-1,3,8-tetraazepi[4.5]deca-2,4-dion bis(1-octyloxy-2,2,6,6-tetramethyl piperidyl)succinate, bis(1-octyloxy-2,2,6,6-tetramethylpiperidyl)succinate, the condensate of N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl)hexamethylene diamine and 4-morpholino-2,6-dichloro-1,3,5-triazine, the condensate of 2-chloro-4,6-di(4-n-butylamino-2,2,6,6-tetramethyl(piperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, the condensate of 2-chloro-4,6-di(4-n-butylamino-1,2,2,6,6-pentamethylpiperidyl)-1,3,5-triazine and 1,2-bis(3-aminopropylamino)ethane, 8-acetyl-3-dodecyl-7,7,9,9-tetramethyl-1,3,8-triaza-azepi[4.5]octane-2,4-dione, 3-dodecyl-1-(2,2,6,6-tetramethyl-4-piperidyl)pyrrolidin-2,5-dione, 3-dodecyl-1-(1,2,2,6,6-pentamethyl-4-piperidyl)pyrrolidin-2,5-dione, a mixture of 4-hexadecyloxy- and 4-stearylxylo-2,2,6,6-tetramethylpiperidine, a condensation product of N,N'-bis-(2,2,6,6-tetramethyl-4-piperidyl)hexamethylene diamine and 4-cyclohexylamino-2,6-dichloro-1,3,5-triazine, a condensation product of 1,2-bis(3-aminopropylamino)ethane and 2,4,6-trichloro-1,3,5-triazine as well as 4-butylamino-2,2,6,6-tetramethylpiperidine (CAS Reg. No. [136514-96-6]), N-(2,2,6,6-tetramethyl-4-piperidyl)-n-dodecylsuccinimid, N-(1,2,2,6,6-pentamethyl-4-piperidyl)-n-dodecylsuccinimid, 2-*n*-octyl-7,7,9,9-tetramethyl-1-oxa-3,8-deca-4-oxo-4,5-dicarbonyl-4,5-dicarbonyl-1-oxa-3,8-diaza-4-oxospiro[4.5]deca-ene and epichlorohydrin.

[0137] 2.7. Oxamides, for example 4,4'-diectoxyxoxanilide, 2,2'-dicinnoxyxoxamide, 2,2'-diectoxy-5,5'-di-tert-butylsuccinimide, 2,2'-di-dodecylxylo-5,5'-di-tert-butoxamide, 2-ethoxy-2'-ethylxoxamide, N,N'-bis(3-dimethylaminocrotonyl)xoxamide, 2-ethoxy-5-tert-butyl-2'-ethoxoxamide and its mixture with 2-ethoxy-2'-ethyl-5,4'-di-tert-butoxamide and mixtures of or no- and para-methoxy-disubstituted oxamides and mixtures of o- and p-ethoxy-disubstituted oxamides.

[0138] 2.8. 2-(2-Hydroxyphenyl)-1,3,5-triazines, for example 2,4,6-tris(2-hydroxy-4-oxyloxyphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-oxyloxyphenyl)-4,6-dis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxyphenyl)-1,3,5-triazine, 2,4-dis(2-hydroxy-4-propyloxyphenyl)-6-(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-octyloxyphenyl)-4,6-dis(4-methylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-dodecylxyloxyphenyl)-4,6-dis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-tridecylxyloxyphenyl)-4,6-dis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-butylxyloxypropoxy)phenyl]-4,6-dis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[4-(dodecylxyloxytridecylxyloxy-2-hydroxypropoxy)-2-hydroxy-phenyl]-4,6-dis(2,4-dimethylphenyl)-1,3,5-triazine, 2-[2-hydroxy-4-(2-hydroxy-3-dodecylxyloxypropoxy)phenyl]-4,6-dis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-hexyloxyphenyl)-4,6-dis(2,4-dimethylphenyl)-1,3,5-triazine, 2-(2-hydroxy-4-methylxyloxyphenyl)-4,6-dis(2,4-dimethylphenyl)-1,3,5-triazine, 2,4,6-tris[2-hydroxy-

dis(2,2,6,6-tetramethyl-4-piperidyl)-1,3,5-triazine, 2-(2-hydroxypropoxy)-4-(4-methoxyphenyl)-6-phenyl-1,3,5-triazine.

[0139] 3. Metal deactivators, for example N,N'-diphenylloxamide, N-salicyl-N'-salicyloyl hydrazine, N,N'-bis(salicyloyl) hydrazine, N,N'-bis(3,5-di-tert-butyl-4-hydroxyphenyl) propionyl) hydrazine, 3-salicyloylamino-1,3,4-triazole, bis(benzyldiene)oxaryl dihydrazide, oxanilide, isophthaloyl dihydrazide, sebacoyl bisphenylhydrazide, N,N'-di-acetylindoyl dihydrazide, N,N'-bis(salicyloyl)oxaryl dihydrazide, N,N'-bis(salicyloyl)-thiopropionyl dihydrazide.

[0140] 4. Phosphites and phosphonites, for example triphenyl phosphite, diphenyl alkyl phosphates, phenyl dialkyl phosphates, tri(nonylphenyl) phosphite, trilauryl phosphite, trioctadecyl phosphite, dilauryl pentacyranoitol diphosphite, tri(2,4-di-tert-butylphenyl) phosphite, diisobutyl pentacyranoitol diphosphite, bis(2,4-di-tert-butylphenyl) pentacyranoitol diphosphite, bis(2,6-di-tert-butyl-4-methylphenyl)-penterythritol diphosphite, diisobutylxylohexyl erythritol diphosphite, bis(2,4-di-tert-butyl-6-methylphenyl) penterythritol diphosphite, bis(2,4,6-tris(tert-butylphenyl) penterythritol diphosphite, triacetyl sorbitol triphosphite, tetraakis(2,4-di-tert-butylphenyl)-4,4'-biphenylene diphosphonic, 6-isooctyl-oxo-2,4,8,10-tetra-tert-butyl-12H-dibenzo[d,g]-1,3,2-dioxaphosphocin, 6-fluoro-2,4,8,10-tetra-tert-butyl-12-methyl-dibenzo[d,g]-1,3,2-dioxaphosphocin, bis(2,4-di-tert-butyl-6-methylphenyl)methylphosphinic, bis(2,4-di-tert-butyl-6-methylphenyl)ethylphosphinic.

[0141] 5. Hydroxylamines, for example, N,N-dibenzylhydroxylamine, N,N-dimethylhydroxylamine, N,N-diethylhydroxylamine, N,N-diisobutyrylhydroxylamine, N,N-distearamidylhydroxylamine, N,N-dihexadecylhydroxylamine, N,N-dioctadecylhydroxylamine, N,N-heptadecyl-N-octadecylhydroxylamine, N,N-eicosylhydroxylamine derived from hydrogenated tall oil amine.

[0142] 6. Nitrones, for example, N-benzyl-alpha-phenylnitroso, N-ethyl-alpha-methyl-nitroso, N-octyl-alpha-betyl-nitroso, N-lauryl-alpha-undecyl-nitroso, N-teradecyl-alpha-tridecyl-nitroso, N-hexadecyl-alpha-pentadecyl-nitroso, N-octadecyl-alpha-heptadecyl-nitroso, N-hexadecyl-alpha-heptadecyl-nitroso, N-octadecyl-alpha-pentadecyl-nitroso, N-heptadecyl-alpha-heptadecyl-nitroso, N-octadecyl-alpha-hexadecyl-nitroso, nitroso derived from N,N-dialkylhydroxylamine derived from hydrogenated tall oil amine.

[0143] 7. Thiosynergists, for example, dilauryl thiodipropionate or dilauryl thiodipropionate

[0144] 8. Peroxide scavengers, for example esters of  $\beta$ -mercaptoisopropanoic acid, for example the lauryl, stearyl, myristyl or undecyl esters, mercaptobenzimidazole or the zinc salt of 2-mercaptobenzimidazole, zinc dibutylthiocarbamate, dioctadecyl disulfide, penterythritol tetrakis( $\beta$ -dodecylmercapto)proionate.

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[0145] 9. Polymeric stabilizers, for example, copper salts in combination with iodides and/or phosphorus compounds and salts of divalent manganese.

[0146] 10. Basic co-stabilizers, for example, melamine, polyvinylpyrrolidone, dicyandiamide, triethyl cyanurate, urea derivatives, hydrazine derivatives, amines, polyamides, polyurethanes, alkali metal salts and alkaline earth metal salts of higher fatty acids for example calcium stearate, zinc stearate, magnesium benenate, magnesium stearate, sodium ricinoleate and potassium palmitate, antimony pyrocatecholate or tin pyrocatecholate.

[0147] 11. Nucleating agents, for example, inorganic substances such as talcum, metal oxides such as titanium dioxide or magnesium oxide, phosphates, carbonates or sulfates of, preferably, alkaline earth metals; organic compounds such as mono- or polycarboxylic acids and the salts thereof, e.g. 4-tert-butylbenzoic acid, adipic acid, dipotassium laetic acid, sodium succinate or sodium benzoate, polymeric compounds such as ionic copolymers ("ionomers")

[0148] 12. Fillers and reinforcing agents, for example, calcium carbonate, silicates, glass fibres, glass bulbs, asbestos, talc, kaolin, mica, barium sulfate, metal oxides and hydroxides, carbon black, graphite, wood flour and flours of fibers of other natural products, synthetic fibers.

[0149] 13. Other additives, for example, plasticizers, lubricants, emulsifiers, pigments, rheology additives, catalysts, flow-control agents, optical brighteners, flameproofing agents, anti-static agents and blowing agents.

[0150] 14. Benzofuranes and indolines, for example those disclosed in U.S. Pat. No. 4,325,863, U.S. Pat. No. 332,244, U.S. Pat. No. 5,175,312, U.S. Pat. No. 5,216,052, U.S. Pat. No. 5,252,543, DE-A-4 316 611, DE-AA 316 622, DE-A-4 316 876, EP-A-0 589 839 or EP-A-0 591 102 or 3-[4-(2-stearoyloxy)hexyl]-5,7-di-tert-butyl-benzofuran-2-one, 5,7-di-tert-butyl-3-[4-(2-stearoyloxyethoxy)phenyl]benzofuran-2-one, 3,3'-bis[5,7-di-tert-butyl-3-(4-[2-hydroxyethoxy]phenyl)benzofuran-2-one], 5,7-di-tert-butyl-3-(4-hydroxyphenyl)benzofuran-2-one, 3-(4-acetoxy-3,S-dimethylphenyl)-5,7-di-tert-butyl-benzofuran-2-one, 3-(3,S-dimethyl-4-pivaloyloxyphenyl)-5,7-di-tert-butyl-benzofuran-2-one.

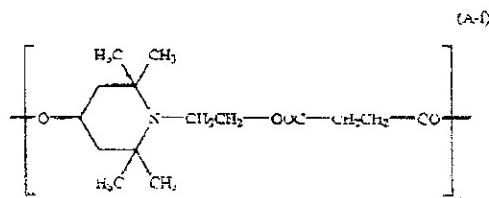
[0151] The weight ratio between the novel stabilizer mixture and the conventional additives can be, for example, from 1:0.5 to 1:5.

[0152] The invention furthermore relates to the use of the novel stabilizer mixture for stabilizing organic materials against oxidative, thermal or light-induced degradation.

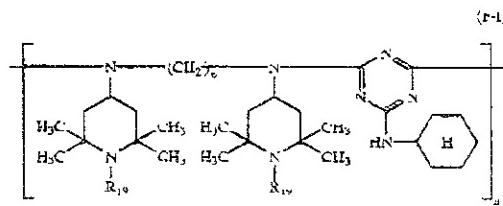
[0153] The organic materials stabilized by means of the novel stabilizer system are distinguished not only by significantly improved light stability, but also in some cases by improved thermal stability.

[0154] The foregoing also applies correspondingly to the following stabilizer mixture, which is likewise a subject-matter of the present invention:

[0155] A stabilizer mixture comprising a compound of the formula A-1



[0156] in which n is a number from 2 to 25, in particular from 2 to 15, and a compound of the formula F-1



[0157] in which R<sub>19</sub> is hydrogen, C<sub>1</sub>-C<sub>2</sub>alkyl, O, -CH<sub>2</sub>CN, C<sub>2</sub>-C<sub>3</sub>alkenyl, C<sub>7</sub>-C<sub>9</sub>phenylalkyl, C<sub>7</sub>-C<sub>9</sub>phenylalkyl which is substituted by C<sub>1</sub>-C<sub>2</sub>alkyl on the phenyl radical, or C<sub>1</sub>-C<sub>2</sub>acyl, and n is a number from 2 to 25, in particular from 2 to 10.

[0158] R<sub>19</sub> is preferably hydrogen or C<sub>1</sub>-C<sub>2</sub>alkyl, in particular hydrogen.

[0159] The individual components of this stabilizer mixture are known and are in some cases commercially available. They can furthermore also be prepared analogously to the processes described in U.S. Pat. No. 4,233,412 and U.S. Pat. No. 4,086,204.

[0160] A stabilizer mixture comprising OTINUVIN 622 and ODASTIB 1082 is preferred.

[0161] The meanings of the terminal groups which saturate the free valences in the compounds of the formulae A-1 and F-1 are dependent on the processes used for their preparation.

[0162] The terminal groups can also be modified after the preparation of the compounds.

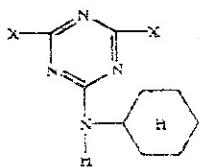
[0163] The comments made regarding the terminal groups of the compounds of the formula I apply correspondingly to the terminal groups of the compound of the formula A-1.

[0164] If the compound of the formula F-1 is prepared by sealing a compound of the formula

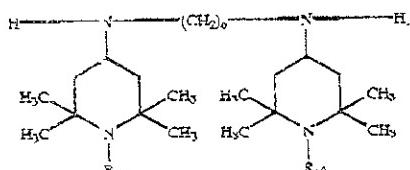
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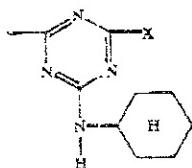
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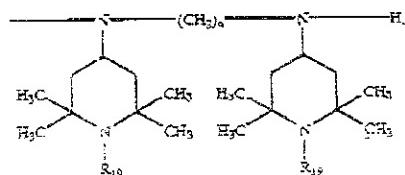
[0165] in which X is, for example, halogen, in particular chlorine, with a compound of the formula



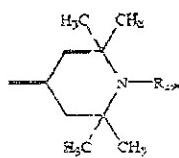
[0166] the terminal group bonded to the diamino radical is hydrogen or



[0167] and the terminal group bonded to the triazine radical is X or



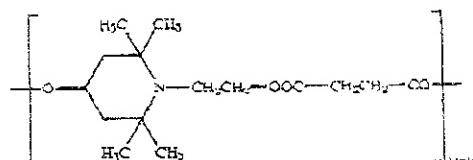
[0168] If X is halogen, it is advantageous to replace this by, for example, -OH or an amino group when the reaction is complete. Examples which may be mentioned of amino groups are: pyrrolidin-1-yl, morpholino, -NH<sub>2</sub>, -N(C<sub>1</sub>-C<sub>6</sub>alkyl)<sub>2</sub> and -NR<sup>5</sup>(C<sub>1</sub>-C<sub>6</sub>alkyl), in which R<sup>5</sup> is hydrogen or a group of the formula



[0169] The examples below illustrate the invention in greater detail. All percentages are by weight, unless stated otherwise.

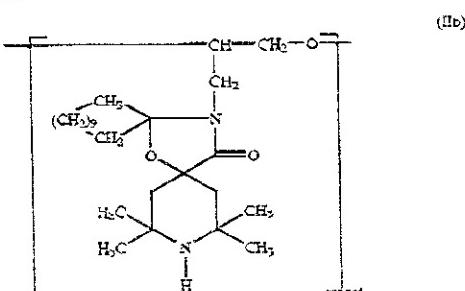
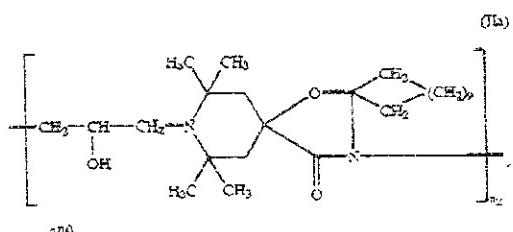
[0170] Light Stabilizers Used in Examples 1-4:

[0171] Compound A:



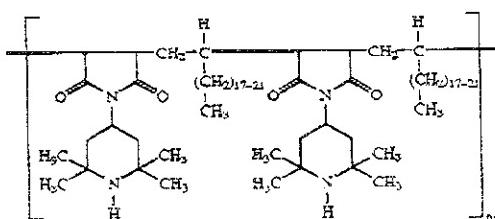
[0172] Compound D:

[0173] Mixture of the compounds



[0174] in which the mean value of n<sub>2</sub> is approx 3.9 and the mean value of n<sub>2'</sub> is approx. 4.2, and the ratio between (Ia) and (Ib) is approx. 4:1

[0175] Compound C-1:



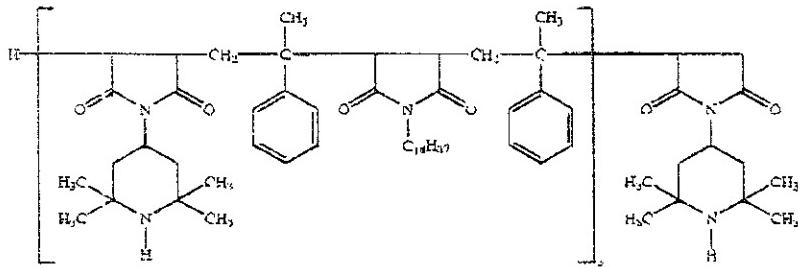
[0176] The mean value of n<sub>2</sub> is 3.2.

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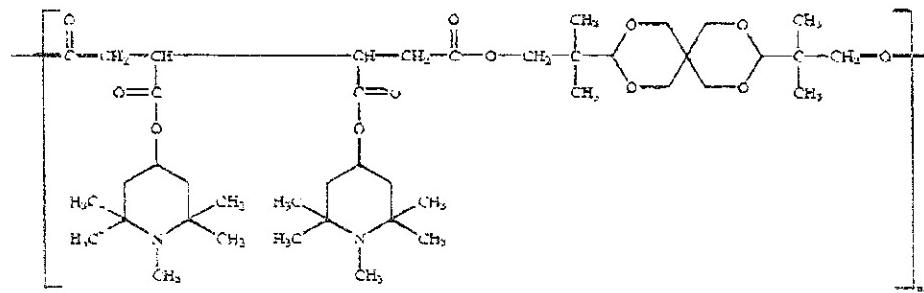
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[0177] Compound C-2:

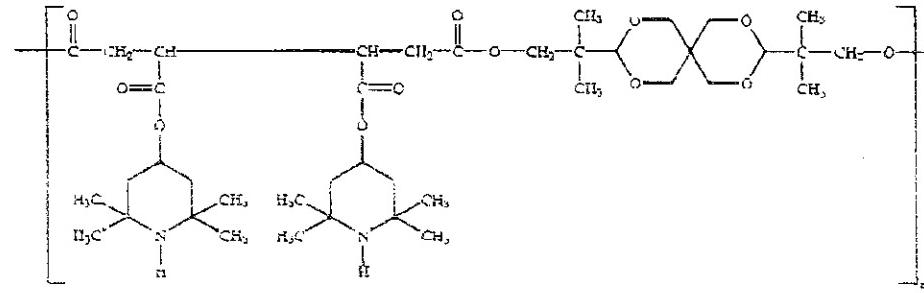


[0178] Compound D-1:



[0179] The mean value of n, is 2.5

[0180] Compound D-2:



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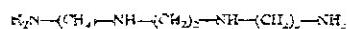
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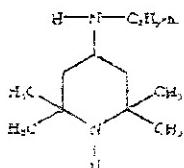
[0181] The mean value of  $n_d$  is 2.5.

[0182] Compound E

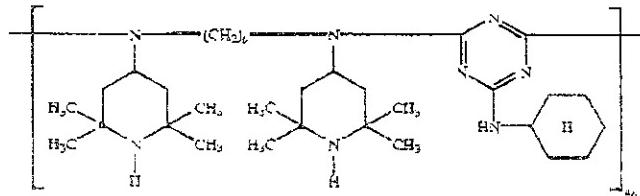
[0183] Product obtainable by reacting a product, obtained by reacting a polyamine of the formula



[0184] with cyanuric chloride, with a compound of the formula



[0185] Compound F

[0186] The mean value of  $n_d$  is 4.4.**EXAMPLE 1****Light Stabilization Action in Polypropylene Tapes**

[0187] 100 parts of polypropylene powder [melt flow index 2.4 g/10 min (230° C., 2100 g)] are mixed in a tumble mixer with 0.05 part of pentacyanobutyl tetrakis[β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.10 part of triis(2,4-di-tert-butylphenyl) phosphate, 0.1 part of calcium stearate and the amount of light stabilizer indicated in Table 1, and the mixture is subsequently granulated in an extruder at a temperature of from 180 to 220° C.

[0188] The granules obtained are converted into a film in a second extruder fitted with a flat film die (temperature from 220 to 260° C.), and the film is cut into tapes, which are subsequently stretched in a ratio of 1.5:2.5 at elevated temperature and wound up (linear density of the tapes from 700 to 900 den; tear strength from 5.5 to 6.5 g/den).

[0189] The polypropylene tapes produced in this way are mounted without tension onto sample carriers and weathered in a WEAVER R-O-METER Ci 65. After various times, 5 test specimens are taken in each case and their tear strength is determined. The measure used for the protective action of the individual light stabilizers is the exposure time before the tear strength of the tapes drops to 50% of the initial value. The values obtained are shown in Table 1.

**TABLE 1**

Light stabilizer	Hours in WEAVER-R-O-METER Ci 65 to 50% of tear strength
None	550
0.1% of compound A	2340
0.1% of compound E	3050
0.05% of compound A and 0.05% of compound E	>3100

**EXAMPLE 2****Light Stabilization Action in Polypropylene Tapes**

[0190] Samples are produced analogously to the process described in Example 1. The tapes are stretched at a ratio of 1:5.25. The experimental results are shown in Table 2.

**TABLE 2**

Light stabilizer	Hours in WEAVER-R-O-METER Ci 65 to 50% residual tear strength	
	0.1% of light stabilizer	0.2% of light stabilizer
None	570	570
Compound A	1730	2900
Compound C-1	1900	3100
Compound C-2	1250	1500
Compound A and compound C-1 in a ratio of 1:1	2350	>3200
Compound A and compound C-2 in a ratio of 1:1	2640	>3200

**EXAMPLE 3****Light Stabilization Action in Polypropylene Block Copolymer Films**

[0191] 100 parts of polypropylene block copolymer powder are homogenized for 10 minutes at 200° C. in a Brabender plastograph with 0.05 part of pentacyanobutyl tetrakis[β-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.10 part of triis(2,4-di-tert-butylphenyl) phosphate, 0.1 part of calcium stearate and the light stabilizers shown in Table 3. The composition obtained is removed from the compounder as rapidly as possible and pressed in a toggle press to give a

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sheet with a thickness of 2-3 mm. A piece of the resultant green pressing is cut out and pressed between two high-gloss hard aluminum foils for 6 minutes at 250°C by means of a hydraulic bench press to give a sheet with a thickness of 0.5 mm, which is immediately cooled in a water-cooled press. Pieces each measuring 60 mm×25 mm are then stamped out of this 0.5 mm sheet and exposed to light in a WEATHER-O-METER Ci 65 (black panel temperature 63±2°C, no exposure to rain water). These test specimens are removed from the exposure apparatus at regular intervals and tested for their carbonyl content in an IR spectrometer. The increase in the carbonyl absorbance during exposure is a measure of the photooxidative degradation of the polymer and is known from experience to be associated with a deterioration in the mechanical properties. The results are shown in Table 3.

TABLE 3

Light stabilizer	Hours in WEATHER-O-METER Ci 65 to 0.2 carbonyl absorbance
0.2% of compound A	2040
0.1% of compound B	1710
0.2% of compound C-1	505
0.2% of compound I	2430
0.2% of compound I'	1550
0.1% of compound A and 0.1% of compound I	3360
0.1% of compound A and 0.1% of compound I'	1540
0.1% of compound C-1 and 0.1% of compound E	3330
0.1% of compound E and 0.1% of compound F	2066
0.1% of compound F	

## EXAMPLE 4

Light Stabilization Action in High-density  
Polyethylene Films

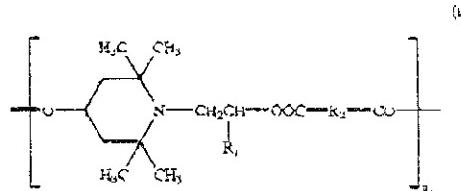
[0192] 100 parts of high-density polyethylene powder (density=0.965 g/cm<sup>3</sup>) are homogenized for 10 minutes at 180°C in a Brabender plasticograph with 0.033 part of pentacrylyltrimethyl[3-(3,5-di-tert-butyl-4-hydroxyphenyl)propionate], 0.066 part of tri(2,4-di-tert-butylphenyl) phosphate, 0.1 part of calcium stearate and the light stabilizers shown in Table 4. The composition is removed from the compounder as rapidly as possible and pressed in a toggle press to give a sheet with a thickness of 2-3 mm. A piece of the resultant green pressing is cut out and pressed between two high-gloss hard aluminum foils for 6 minutes at 210°C by means of a hydraulic bench press to give a sheet with a thickness of 0.5 mm, which is immediately cooled in a water-cooled press. Pieces measuring 60 mm×25 mm are then stamped out of this 0.5 mm sheet and exposed to light in a Weather-O-meter Ci 65 (black panel temperature 63±2°C, no exposure to rain water). These test specimens are removed from the exposure apparatus at regular intervals and tested for their vinyl content in an IR spectrometer. The increase in the vinyl absorbance (909 cm<sup>-1</sup>) during exposure is a measure of the photooxidative degradation of the polymer and is known from experience to be associated with a deterioration in the mechanical properties. The results are shown in Table 4.

TABLE 4

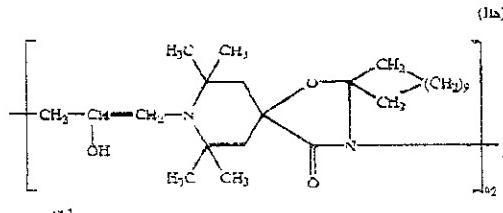
Light stabilizer	Vinyl absorbance after 7222 hours in the WEATHER-O-METER Ci 65
None	0.092 4741 318 hours
0.1% of compound A	0.053
0.1% of compound B	0.043
0.1% of compound C-1	0.038
0.1% of compound C-1	0.143 after 5288 hours
0.1% of compound D-1	0.040
0.1% of compound D-2	0.040
0.1% of compound E	0.054
0.1% of compound F	0.051
0.05% of compound A and 0.05% of compound B	0.030
0.05% of compound A and 0.05% of compound C-1	0.033
0.05% of compound A and 0.05% of compound C-2	0.029
0.05% of compound A and 0.04% of compound D-1	0.037
0.05% of compound A and 0.05% of compound D-2	0.034
0.05% of compound A and 0.05% of compound E	0.037
0.05% of compound A and 0.05% of compound F	0.037
0.05% of compound F	

What is claimed is

1. A stabilizer mixture comprising a component a) and a component b), c), d) or e), where  
component a) is at least one compound of the formula i

in which R<sub>1</sub> is hydrogen or methyl;R<sub>2</sub> is a direct bond or C<sub>1</sub>-C<sub>n</sub>alkylene and

n is a number from 2 to 50;

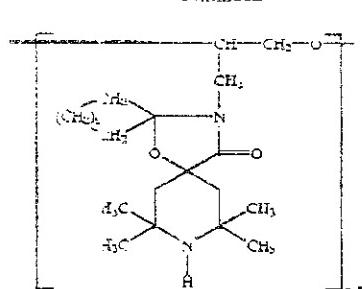
component b) is at least one compound of the formulae IIa  
and IIb

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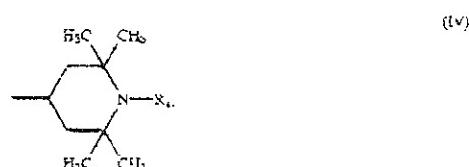
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in which R<sub>3</sub> and R<sub>4</sub>, independently of one another, are a direct bond or an —N(X<sub>1</sub>)—CO—X<sub>2</sub>—CO—N(X<sub>3</sub>)—group, where X<sub>1</sub> and X<sub>3</sub>, independently of one another, are hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl, phenyl, C<sub>7</sub>-C<sub>12</sub>phenylalkyl or a group of the formula IV



in which n<sub>1</sub> and n<sub>2</sub> are a number from 2 to 50;

component c) is at least one compound of the formula III

and X<sub>2</sub> is a direct bond or C<sub>1</sub>-C<sub>6</sub>alkylene,

R<sub>3</sub> is hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, O—CH<sub>2</sub>CN, C<sub>5</sub>-C<sub>12</sub>alkenyl, C<sub>7</sub>-C<sub>12</sub>phenylalkyl,

C<sub>7</sub>-C<sub>12</sub>phenylalkyl which is substituted by C<sub>1</sub>-C<sub>6</sub>alkyl on the phenyl radical, or C<sub>2</sub>-C<sub>6</sub>acyl.

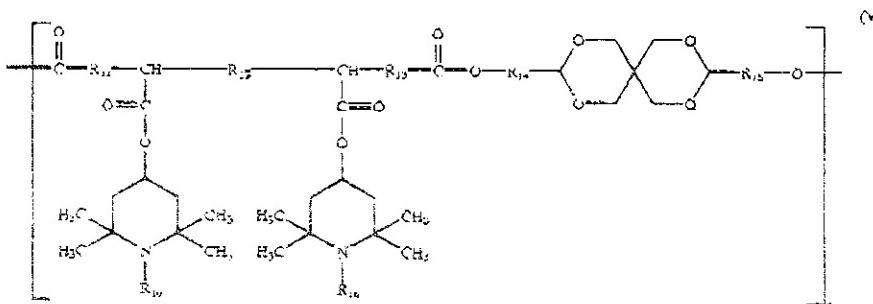
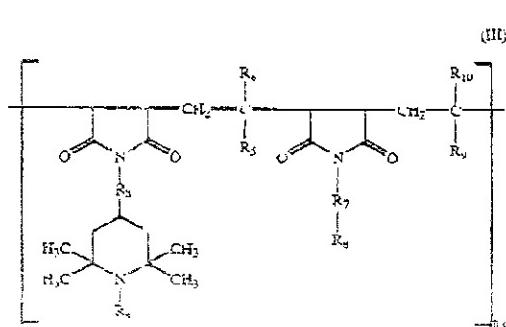
R<sub>2</sub>, R<sub>3</sub>, R<sub>5</sub> and R<sub>10</sub>, independently of one another, are hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl,

C<sub>5</sub>-C<sub>12</sub>cycloalkyl or phenyl,

R<sub>9</sub> is hydrogen, C<sub>1</sub>-C<sub>6</sub>alkyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl, C<sub>7</sub>-C<sub>12</sub>phenylalkyl, phenyl or a group of the formula IV, and

n<sub>2</sub> is a number from 1 to 50;

component d) is at least one compound of the formula V



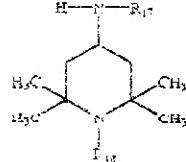
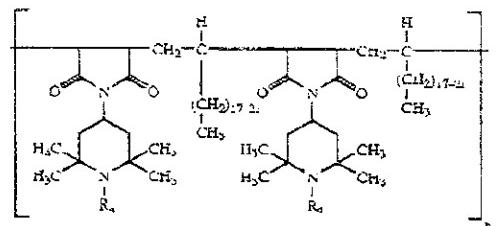
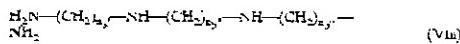
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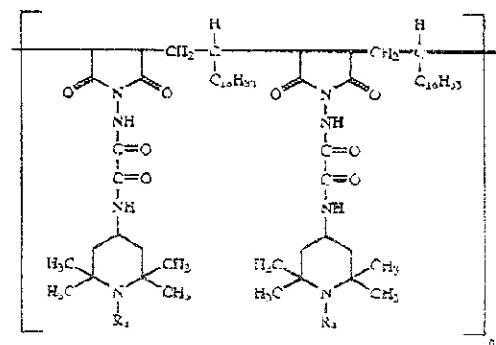
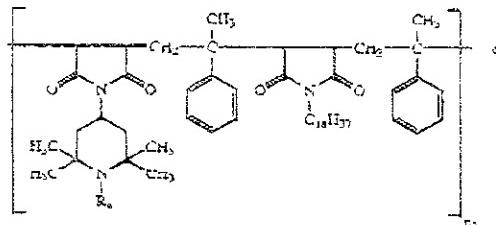
19

in which R<sub>11</sub>, R<sub>12</sub>, R<sub>13</sub>, R<sub>14</sub>, and R<sub>15</sub>, independently of one another, are a direct bond or C<sub>1</sub>-C<sub>20</sub>alkylene, R<sub>16</sub> is as defined for R<sub>6</sub> and n<sub>6</sub> is a number from 1 to 50; and

component u) is a product obtainable by reacting a product, obtained by reacting a polyamine of the formula VIa with cyanuric chloride, with a compound of the formula VIb



(VIb)



in which n<sub>1</sub>, n<sub>2</sub>, and n<sub>3</sub>, independently of one another, are a number from 2 to 12, R<sub>7</sub> is hydrogen, C<sub>1</sub>-C<sub>12</sub>alkyl, C<sub>5</sub>-C<sub>12</sub>cycloalkyl, phenyl or C<sub>7</sub>-C<sub>12</sub>phenylalkyl, and R<sub>8</sub> is as defined for R<sub>2</sub>.

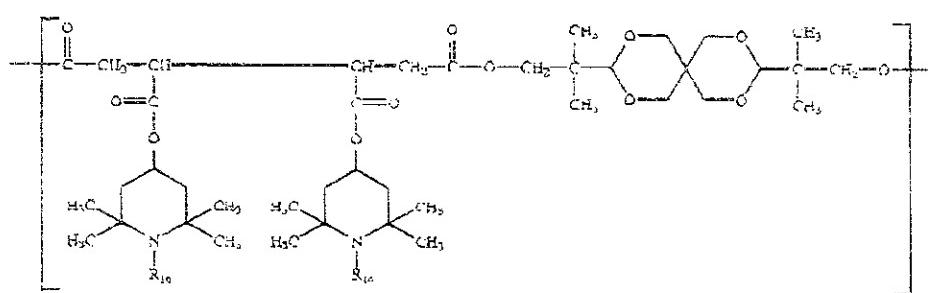
2. A stabilizer mixture according to claim 1, in which R<sub>1</sub> is hydrogen, R<sub>2</sub> is ethylene and n<sub>1</sub> is a number from 2 to 25.

3. A stabilizer mixture according to claim 1, in which R<sub>2</sub> and R<sub>7</sub> are a direct bond or an -N(X<sub>1</sub>)—CO—X<sub>2</sub>—CO—N(X<sub>3</sub>)— group, where X<sub>1</sub> and X<sub>3</sub>, independently of one another, are hydrogen or C<sub>1</sub>-C<sub>2</sub>alkyl and X<sub>2</sub> is a direct bond, R<sub>1</sub> is hydrogen, C<sub>1</sub>-C<sub>4</sub>alkyl, OH, C<sub>1</sub>-C<sub>2</sub>alkoxy, C<sub>2</sub>-C<sub>2</sub>cycloalkoxy, silyl, benzyl or acetyl, R<sub>5</sub> and R<sub>6</sub> are C<sub>1</sub>-C<sub>2</sub>alkyl or phenyl, R<sub>9</sub> and R<sub>10</sub> are hydrogen or C<sub>1</sub>-C<sub>2</sub>alkyl, R<sub>6</sub> is C<sub>1</sub>-C<sub>2</sub>alkyl or a group of the formula IV, R<sub>11</sub>, R<sub>13</sub>, R<sub>14</sub> and R<sub>15</sub> are C<sub>1</sub>-C<sub>2</sub>alkylclic, R<sub>12</sub> is a direct bond, and R<sub>16</sub> is as defined for R<sub>4</sub>.

4. A stabilizer mixture according to claim 1, in which component c) is at least one compound of the formula

in which R<sub>1</sub> is hydrogen or methyl, and n<sub>3</sub> is a number from 1 to 50

5. A stabilizer mixture according to claim 1, in which component d) is at least one compound of the formula



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in which  $R_{16}$  is hydrogen or methyl, and  $n_5$  is a number from 1 to 50.

6. A stabilizer mixture according to claim 1, in which  $n_5$ ,  $n_5'$  and  $n_5''$ , independently of one another, are a number from 2 to 4,  $R_{17}$  is  $C_1-C_6$ alkyl, and  $R_{18}$  is hydrogen.

7. A stabilizer mixture according to claim 1, which comprises components a) and b).

8. A stabilizer mixture according to claim 1, which comprises components a) and c).

9. A stabilizer mixture according to claim 1, which comprises components a) and d)

10. A stabilizer mixture according to claim 1, which comprises components a) and e)

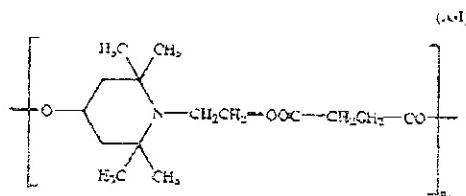
11. A composition comprising an organic material which is sensitive to oxidative, thermal or light-induced degradation and a stabilizer mixture according to claim 1

12. A composition according to claim 11, in which the organic material is a polyolefin

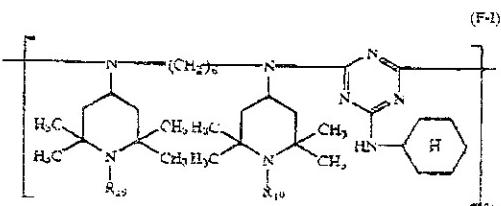
13. A composition according to claim 11, in which the organic material is polyethylene, polypropylene or a copolymer of polyethylene or polypropylene.

14. A process for stabilizing an organic material which is sensitive to oxidative, thermal or light-induced degradation, which comprises incorporating a stabilizer mixture according to claim 1 into the organic material

15. A stabilizer mixture comprising a compound of the formula A-1,



in which  $n_1$  is a number from 2 to 25, and a compound of the formula F-1,



in which  $R_{19}$  is hydrogen,  $C_1-C_6$ alkyl,  $O,-CH_2CN$ ,  $C_3-C_6$ alkenyl,  $C_7-C_9$ phenylalkyl,  $C_7-C_9$ phenylalkyl which is substituted by  $C_1-C_6$ alkyl on the phenyl radical, or  $C_1-C_6$ acyl, and  $n_2$  is a number from 2 to 25

\* \* \* \* \*

## CIVIL COVER SHEET

The JS-44 civil cover sheet and the information contained herein neither replace nor supplement the filing and service of pleadings or other papers as required by law, except as provided by local rules of court. This form, approved by the Judicial Conference of the United States in September 1974, is required for the use of the Clerk of Court for the purpose of initiating the civil docket sheet. (SEE INSTRUCTIONS ON THE REVERSE OF THE FORM.)

## I. (a) PLAINTIFFS

Ciba Specialty Chemicals Corporation

(b) County of Residence of First Listed Plaintiff San Mateo County, CA  
(EXCEPT IN U.S. PLAINTIFF CASES)

(c) Attorney's (Firm Name, Address, and Telephone Number)

Chad M. Shandler  
Richards, Layton & Finger  
One Rodney Square  
920 North King Street  
Wilmington, DE 19801  
302-651-7700

## DEFENDANTS

3V, Inc.

County of Residence of First Listed Defendant New Castle County, DE  
(IN U.S. PLAINTIFF CASES ONLY)

NOTE: IN LAND CONDEMNATION CASES, USE THE LOCATION OF THE LAND INVOLVED

Attorneys (If Known)

## II. BASIS OF JURISDICTION (Place an "X" in One Box Only)

- |  |  |
|--|--|
| <input type="checkbox"/> 1 U.S. Government Plaintiff | <input checked="" type="checkbox"/> 3 Federal Question (U.S. Government Not a Party) |
| <input type="checkbox"/> 2 U.S. Government Defendant | <input type="checkbox"/> 4 Diversity (Indicate Citizenship of Parties in Item III)   |

## III. CITIZENSHIP OF PRINCIPAL PARTIES (Place an "X" in One Box for Plaintiff and One Box for Defendant)

	PTF	DEF	PTF	DEF
Citizen of This State	<input type="checkbox"/> 1	<input type="checkbox"/> 1	Incorporated or Principal Place of Business In This State	<input type="checkbox"/> 4 <input checked="" type="checkbox"/> 4
Citizen of Another State	<input type="checkbox"/> 2	<input type="checkbox"/> 2	Incorporated and Principal Place of Business In Another State	<input type="checkbox"/> 5 <input type="checkbox"/> 5
Citizen or Subject of a Foreign Country	<input type="checkbox"/> 3	<input type="checkbox"/> 3	Foreign Nation	<input type="checkbox"/> 6 <input type="checkbox"/> 6

## IV. NATURE OF SUIT (Place an "X" in One Box Only)

CONTRACT	TORTS	FORFEITURE/PENALTY	BANKRUPTCY	OTHER STATUTES
<input type="checkbox"/> 110 Insurance	<input type="checkbox"/> PERSONAL INJURY	<input type="checkbox"/> PERSONAL INJURY	<input type="checkbox"/> 610 Agriculture	<input type="checkbox"/> 400 State Reappointment
<input type="checkbox"/> 120 Marine	<input type="checkbox"/> 310 Airplane	<input type="checkbox"/> 362 Personal Injury - Med. Malpractice	<input type="checkbox"/> 620 Other Food & Drug	<input type="checkbox"/> 410 Antitrust
<input type="checkbox"/> 130 Miller Act	<input type="checkbox"/> 315 Airplane Product Liability	<input type="checkbox"/> 365 Personal Injury - Product Liability	<input type="checkbox"/> 625 Drug Related Seizure of Property 21 USC 881	<input type="checkbox"/> 430 Banks and Banking
<input type="checkbox"/> 140 Negotiable Instrument	<input type="checkbox"/> 320 Assault, Libel & Slander	<input type="checkbox"/> 368 Asbestos Personal Injury Product Liability	<input type="checkbox"/> 630 Liquor Laws	<input type="checkbox"/> 450 Commerce
<input type="checkbox"/> 150 Recovery of Overpayment & Enforcement of Judgment	<input type="checkbox"/> 330 Federal Employers' Liability	<input type="checkbox"/> PERSONAL PROPERTY	<input type="checkbox"/> 640 R.R. & Truck	<input type="checkbox"/> 460 Deportation
<input type="checkbox"/> 151 Medicare Act	<input type="checkbox"/> 340 Marine	<input type="checkbox"/> 370 Other Fraud	<input type="checkbox"/> 650 Airline Regs	<input type="checkbox"/> 470 Racketeer Influenced and Corrupt Organizations
<input type="checkbox"/> 152 Recovery of Defaulted Student Loans (excl Veterans)	<input type="checkbox"/> 345 Marine Product Liability	<input type="checkbox"/> 371 Truth In Lending	<input type="checkbox"/> 660 Occupational Safety/Health	<input type="checkbox"/> 480 Consumer Credit
<input type="checkbox"/> 153 Recovery of Overpayment of Veteran's Benefits	<input type="checkbox"/> 350 Motor Vehicle	<input type="checkbox"/> 380 Other Personal Property Damage	<input type="checkbox"/> 690 Other	<input type="checkbox"/> 490 Cable/Sat TV
<input type="checkbox"/> 160 Stockholder's Suits	<input type="checkbox"/> 355 Motor Vehicle Product Liability	<input type="checkbox"/> 385 Property Damage Product Liability	<input type="checkbox"/> LABOR	<input type="checkbox"/> 510 HIA (1395f)
<input type="checkbox"/> 190 Other Contract	<input type="checkbox"/> 360 Other Personal Injury	<input type="checkbox"/> PRISONER PETITIONS	<input type="checkbox"/> 710 Fair Labor Standards Act	<input type="checkbox"/> 520 Black Lung (923)
<input type="checkbox"/> 195 Contract Product Liability	<input type="checkbox"/> CIVIL RIGHTS	<input type="checkbox"/> 510 Motions to Vacate Sentence Habeas Corpus:	<input type="checkbox"/> 720 Labor/Mgmt Relations	<input type="checkbox"/> 530 DIWC/DIWW (405(g))
<input type="checkbox"/> 196 Franchise	<input type="checkbox"/> 441 Voting	<input type="checkbox"/> 530 General	<input type="checkbox"/> 730 Labor/Mgmt Reporting & Disclosure Act	<input type="checkbox"/> 540 SSID Title XVI
<b>REAL PROPERTY</b>	<input type="checkbox"/> 442 Employment	<input type="checkbox"/> 535 Death Penalty	<input type="checkbox"/> 740 Railway Labor Act	<input type="checkbox"/> 550 RSI (405(g))
<input type="checkbox"/> 210 Land Condemnation	<input type="checkbox"/> 443 Housing/ Accommodations	<input type="checkbox"/> 540 Mandamus & Other	<input type="checkbox"/> 790 Other Labor Litigation	<input type="checkbox"/> 560 Taxes (U.S. Plaintiff or Defendant)
<input type="checkbox"/> 220 Foreclosure	<input type="checkbox"/> 444 Welfare	<input type="checkbox"/> 550 Civil Rights	<input type="checkbox"/> 791 Empl Ret Inc Security Act	<input type="checkbox"/> 570 IRS - Third Party
<input type="checkbox"/> 230 Rent Lease & Eject	<input type="checkbox"/> 445 Amer. w/Disabilities - Employment	<input type="checkbox"/> 555 Prison Condition		<input type="checkbox"/> 580 26 USC 7609
<input type="checkbox"/> 240 Torts to Land	<input type="checkbox"/> 446 Amer. w/Disabilities - Other			
<input type="checkbox"/> 245 Tort Product Liability	<input type="checkbox"/> 440 Other Civil Rights			
<input type="checkbox"/> 290 All Other Real Property				

## V. ORIGIN

(Place an "X" in One Box Only)

<input checked="" type="checkbox"/> Original Proceeding	<input type="checkbox"/> 2 Removed from State Court	<input type="checkbox"/> 3 Remanded from Appellate Court	<input type="checkbox"/> 4 Reinstated or Reopened	<input type="checkbox"/> 5 Transferred from another district (specify) _____	<input type="checkbox"/> 6 Multidistrict Litigation	<input type="checkbox"/> 7 Appeal to District Judge from Magistrate Justice
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## VI. CAUSE OF ACTION

Cite the U.S. Civil Statute under which you are filing (Do not cite jurisdictional statutes unless diversity): 35 U.S.C. §146; 37 C.F.R. §31.303

Brief description of cause: Action under patent laws for declaratory relief

## VII. REQUESTED IN COMPLAINT

 CHECK IF THIS IS A CLASS ACTION UNDER F.R.C.P. 23

DEMAND'S

CHECK YES only if demanded in complaint:  
JURY DEMAND:  Yes  NoVIII. RELATED CASE(S)  
IF ANY

(See instructions):

JUDGE

Joseph J. Farnan, Jr.

DOCKET NUMBER

06-00593-JJF

DATE October 10, 2006

SIGNATURE OF ATTORNEY OF RECORD

FOR OFFICE USE ONLY  
RECEIPT # \_\_\_\_\_ AMOUNT \_\_\_\_\_ APPLYING IPP \_\_\_\_\_ JUDGE \_\_\_\_\_ MAG JUDGE \_\_\_\_\_

AO FORM 85 RECEIPT (REV. 9/04)

United States District Court for the District of Delaware

Civil Action No.

06-929

**ACKNOWLEDGMENT**  
**OF RECEIPT FOR AO FORM 85**

**NOTICE OF AVAILABILITY OF A**  
**UNITED STATES MAGISTRATE JUDGE**  
**TO EXERCISE JURISDICTION**

I HEREBY ACKNOWLEDGE RECEIPT OF \_\_\_\_\_ COPIES OF AO FORM 85.

10/10/06

(Date forms issued)

Matthew G. Marin

(Signature of Party or their Representative)

(Printed name of Party or their Representative)

Note: Completed receipt will be filed in the Civil Action